

THE RELATIONSHIP BETWEEN NICKEL TOXICITY AND MAJOR NUTRIENT SUPPLY

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INTRODUCTION

In several small areas of Aberdeenshire, cereal crops are seriously affected by nickel toxicity, resulting from the abnormally high nickel content of the soils. The soils are derived from a mixed drift in which serpentine predominates; the two main soil types which can be distinguished are an acid peat (pH 4.5–5.3) on the low ground, and a loam or peaty loam (pH 5.6–6.7) on hill slopes. The phosphorus and potassium status of both is low, calcium is satisfactory and magnesium high; the manganese status of the hill soils is low.

The symptoms of nickel toxicity vary with plant species but a general feature, in common with excesses of other heavy metals, is the production of an induced iron deficiency. The oat plant is particularly sensitive to excess nickel, which produces longitudinal white stripes of necrotic tissue in the leaves of affected plants, which are also to some degree chlorotic. The symptoms and anatomical changes induced in the oat plant by toxic levels of nickel and cobalt have recently been described; the anatomical changes have been shown to be similar to those accompanying iron deficiency (Vergnano and Hunter¹³).

Field experiments carried out by Hunter and Vergnano⁸) showed that the most satisfactory corrective treatment for these nickel-toxic soils is the application of lime, the resulting reduction in toxicity symptoms being due to reduced availability of soil nickel. In the course of further investigations using soil and sand cultures, certain discrepancies were observed in the results obtained. This suggested the existence of a relationship between the effect of nickel and the supply of major nutrients, a possibility strengthened

by the abundant evidence of a similar relationship existing between major elements (especially calcium) and certain other trace elements (for example, manganese and aluminium, Hewitt⁵)).

Subsequent experiments carried out by Vergnano¹¹)¹²) indicated that a high level supply of calcium to oats in sand culture reduced the necrotic symptoms due to nickel, a result comparable with that seen in the field. On the other hand an increase in the amount of phosphorus supplied caused an increase in the degree of symptoms.

The experiments described in this paper were therefore designed to establish the relationship between level of supply of major nutrients and nickel toxicity in sand-cultured oat plants. The results would be used to assess the effect of variation in major-element supply on (a) absorption of nickel, (b) level of toxic symptoms produced and (c) reduction in yield due to nickel. The effect of nickel on the absorption of major elements would also be examined.

EXPERIMENTAL

Sand rather than soil cultures were used so that the nutrient relations might be less complex, thus facilitating interpretation of results. A factorial design was used involving two levels (normal and high) of each of the five major nutrients (nitrogen, phosphorus, potassium, calcium, and magnesium) and two levels of nickel (0, and 2.5 ppm). All combinations of these six, two-level factors gave 64 treatments and each was applied to a unit of 3 pots. Three of the third-order interactions, NPKNi, NCaMgNi and PKCaMg, were confounded with blocks to allow the 64 treatment units to be arranged in four blocks of 16. The usual randomisation procedure was carried out in allocating groups of treatments to the blocks, and treatments to the units within a block. Since only one replication was used an estimate of experimental error with 19 degrees of freedom was obtained from the remaining third-order and higher-order interactions.

Oats (variety "Victory") were grown in coarse quartz sand (13% held by 14-mesh and 99% by 30-mesh British standard sieve) in 9" clay pots coated with bituminous paint. Traces of the major elements were removed from the sand by successive washings with hot 15% hydrochloric acid. Adsorbed hydrogen ions were subsequently

removed by intermittent application over 4 days of the nutrient solutions later to be supplied to the plants. Seeds were sown in the damp sand and water was supplied until the shoots were $\frac{1}{4}$ " high. Thereafter appropriate nutrient solutions were given twice daily in adequate amounts. Before each application of solution the sand was flushed with water to remove the residue from the previous addition.

The nutrient solutions were prepared by adding measured volumes of stock solutions to water and diluting with water to a predetermined volume. The composition per litre of the major-element stock solutions, and volumes required to prepare 10 litres of each nutrient solution are given in Table I. The table is given as concisely as possible, but it is understood that 32 solutions were involved, produced by varying each of the major nutrients one at a time. *E.g.* in the treatment $N_2P_1K_2Ca_1Mg_1$ the amounts of stock solution for P, Ca and Mg would be found under "normal" and those for N and K under "high". "Normal" and "high" correspond to "level 1" and "level 2" respectively which are used in reporting results.

TABLE I

Composition of nutrient solutions					
Salt	g/l	"Normal"		"High"	
		ml/10 l	ppm of element	ml/10 l	ppm of element
$NaNO_3$	250	15	138 *)	75	310 *)
$Na_2HPO_4 \cdot 12H_2O$	50	20	8.7	140	61
K_2SO_4	90	20	81	120	486
$Ca(NO_3)_2 \cdot 4H_2O$	430	15	151 †)	15	602 †)
$CaCl_2$	453	2.5	—	30	—
$MgSO_4 \cdot 7H_2O$	250	15	37	75	185

*) including N supplied by $Ca(NO_3)_2 \cdot 4H_2O$.

†) including Ca supplied by $CaCl_2$.

A basic level of trace elements was included by the addition of 10 ml of a stock solution containing (per l) 6.40 g ferric citrate, 0.98 g $MnSO_4 \cdot 4H_2O$, 0.04 g $CuSO_4 \cdot 5H_2O$, and 0.35 g H_3BO_3 . The concentration of trace elements was therefore Fe, 1.2 ppm; Mn, 0.24 ppm; Cu, 0.01 ppm; B, 0.06 ppm. Nickel was supplied as the sulphate. The pH of each solution was adjusted by sulphuric acid to 5.5.

The experiment was carried out during the summer in a bird-proof cage. Plants were thinned to 80 per pot at an early stage and heights and toxic symptoms were recorded from time to time. The plants

were grown for 34 days before harvesting. Plants were weighed fresh, and then again after drying at 80°C; major elements, iron and nickel were determined in the dry matter and expressed on a total uptake basis. The analytical methods used were: nitrogen: Kjeldahl macro-digestion followed by modified Conway micro-diffusion; potassium and calcium: flame photometer; phosphorus: colorimetric molybdenum blue using hydrazine sulphate; magnesium: colorimetric thiazol yellow (Hunter⁷); iron: colorimetric α , α -dipyridyl; nickel: colorimetric dimethylglyoxime.

Two further subsidiary sand-culture experiments using oats were carried out in which major elements were supplied at "normal" (the same level as that used in the main factorial experiment) and "low" level while nickel was supplied at 0, 2.5 or 5 ppm in the nutrient solution. Both experiments ran for 40 days. In the first, nickel was supplied for the whole period from germination; while in the second, the plants received nickel during the last 10 days only. Differences in degree of toxic symptoms between treatments in the first experiment had been small, especially at the 5 ppm nickel level, and by adopting the second procedure it was hoped to produce a wider range of symptoms. In practice this hope was realised, and when nickel was supplied to plants which had been raised on nutrient solutions low in any one of the major nutrients the rate of symptom production and degree of toxicity varied widely.

RESULTS

In order to present the results in as concise a form as possible, tables have been drawn up which are derived from a statistical analysis of the full analytical data. Their layout is explained under the relevant heading.

Yield

In the yield tables given below, the left-hand table shows the effect of change in level of supply of major nutrients on yield. The entries are thus means of 32 observations, *e.g.* 83.3 g is the mean yield of the 32 treatments receiving nitrogen at the lower level. Similarly the yield of 100.9 g is the mean derived from the 32 N₂ treatments. The right-hand table gives the reduction in yield due to nickel at the two levels of each of the major nutrients.

TABLE II

Yield of dry matter (g) per treatment					
Factor	Mean yield (g)		Factor	Nickel effect (—11.9 g)	
	level of factor			level of factor	
	1	2		1	2
N	83.3	100.9 *)	N	—13.0	—10.8
P	86.8	97.5 *)	P	— 8.8	—15.0 §)
K	90.2	94.1 †)	K	—14.7	— 9.1 §)
Ca	93.0	91.3	Ca	—15.9	— 7.9 †)
Mg	93.8	90.4 §)	Mg	—13.9	— 9.9
Ni	98.1	86.2 *)			
SE of difference = + 1.2			SE of differences = + 2.4		

*) Significant at 0.1% level. †) Significant at 1% level. §) Significant at 5% level.

When variation in yield due to differences in major-element supply was examined it was found that nitrogen, phosphorus and potassium increased yield while magnesium reduced it. With the addition of nickel a marked reduction in yield resulted. Increase in calcium and potassium offset this reduction in yield due to nickel but increase in phosphorus supply produced a further decrease.

Nickel toxic symptoms

Signs of nickel toxicity first appeared two weeks after the start of the experiment. It was noticed that symptoms in high phosphorus treatments were generally more severe than in corresponding low phosphorus treatments, and that high nitrogen and calcium had reduced the degree of necrosis. Marks were allotted on the scale of 0 (no symptoms) to 10 (very severe necrosis). When the experiment was harvested only treatment $N_1P_2K_1Ca_1Mg_1$ rated 10 while certain treatments involving high nitrogen and calcium had scores of only 2 or 3. The control treatment with major nutrients supplied at normal level scored 9. In the absence of applied nickel no symptoms were observed. The data thus consisted of observations on the 32 treatments which had received nickel. Analysis of variance was carried out on these visual scores and an estimate of error variance with 13 degrees of freedom was derived from high-order interactions. The results in Table III show the effects of the five major nutrients on necrotic symptoms. The figures given in the table are the mean of 16 observations at each level of the factors.

TABLE III

Nickel toxic symptoms (necrosis)		
Factor	Mean score	
	level of factor	
	1	2
N	4.6	1.6 *)
P	2.6	3.6 †)
K	3.7	2.5 †)
Ca	4.1	2.1 *)
Mg	4.2	2.0 *)
SE of difference = ± 0.34		

An increase in nitrogen, calcium or magnesium supply has given large reductions in necrotic symptoms. Increase in potassium supply also significantly reduced the necrotic symptoms. In contrast to these results, phosphorus has had the opposite effect and increased the symptoms.

Chlorotic symptoms were also recorded and marks were allotted on a scale 0 (no symptoms) to 5 (severe chlorosis). Data were obtained only for these treatments which received nickel. Mean values for the two levels of each factor are given in Table IV.

TABLE IV

Nickel toxic symptoms (chlorosis)		
Factor	Mean score	
	level of factor	
	1	2
N	3.1	2.1 †)
P	1.8	3.4 *)
K	2.6	2.5
Ca	2.7	2.4
Mg	2.8	2.4
SE of difference = ± 0.25		

Phosphorus was found to increase chlorosis but increase in the major-element cations did not significantly affect the level of chlorosis. Nitrogen, however, was found to reduce chlorosis but this result should be treated with some reserve, in view of the possibility that chlorosis was masked in high-nitrogen plants. In the analyses of the two sets of scores the error variances appeared homogeneous. In the case of necrotic scores a more rigorous analysis was carried out. The results of this analysis confirmed those already given.

Analytical Results

The plant analyses exhibited features common to most nutrition experiments; a higher level of an element in the nutrient solution resulted in an increased concentration of that element in the plant, and sometimes caused a reduction in the uptake of other ions. No useful purpose is served by reporting these major-element interactions in full since they are merely incidental to the main investigation. Table V contains the relevant analytical data. The upper part of the table sets out the effect of nickel on the mean uptakes of each of the major elements and iron. In the lower part this nickel effect is examined in terms of variation in major nutrient supply.

The uptake of iron and the major elements (with the exception of calcium) has been markedly reduced by nickel. Where nickel reduced the uptake of an element the effect was generally greater when the element was supplied at the higher level (phosphorus and potassium) although with magnesium the effect was greater at the lower level of magnesium supply. The increase in uptake of calcium due to nickel was greater where high calcium was supplied.

Turning to other first-order interactions, reductions in nitrogen and phosphorus uptake were offset by a high level supply of potassium, while reduction in potassium uptake produced by nickel was less where calcium or magnesium supply was high. A similar effect was produced by high level magnesium on the reduced iron uptake.

Values for nickel uptake at the two levels of each of the major nutrients were obtained from the 32 treatments where nickel was supplied. Where no nickel was supplied that found in the plants was derived from the nickel present as an impurity in the nutrient salts used. The average uptake for the 32 (no-nickel) treatments was 0.70 mg in contrast to an average uptake of 6.55 mg by plants supplied with 2.5 ppm nickel in the nutrient solution. Variation in the level of supply of the major nutrients, except phosphorus, had no great effect on the uptake of nickel. Phosphorus, however, significantly increased the uptake of nickel, a finding in agreement with the increased severity of symptoms resulting on an increase in the level of supply of substrate phosphorus.

Results of subsidiary experiments

As was mentioned earlier, toxic symptoms produced in the first

TABLE V

Mean uptake (g)														
	Nitrogen		Phosphorus		Potassium		Calcium		Magnesium		Iron (mg)		Nickel (mg)	
Level of factor	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Factor														
Ni														
SE of difference	3.72	3.22 *	0.629	0.534**	4.31	3.65*	0.280	0.317*	0.238	0.220*	2.33	1.67*	—	—
	± 0.052		± 0.0094		± 0.053		± 0.0040		± 0.0043		± 0.089		± 0.089	
Nickel effect	—0.50 g		—0.095 g		—0.66 g		0.037 g		—0.018 g		—0.66 mg		—	
N	—0.58	—0.42	—0.111	—0.079	—0.76	—0.56	0.039	0.035	—0.016	—0.020	—0.65	—0.67	6.55	6.56
P	—0.44	—0.56	—0.041	—0.149*	—0.60	—0.72	0.036	0.038	—0.015	—0.021	—0.53	—0.79	6.21	6.90 †
K	—0.67	—0.33§	—0.123	—0.067†	—0.53	—0.79§	0.037	0.037	—0.025	—0.011	—0.74	—0.58	6.51	6.60
Ca	—0.60	—0.40	—0.109	—0.081	—0.78	—0.54§	0.016	0.058*	—0.017	—0.019	—0.81	—0.51	6.36	6.75
Mg	—0.54	—0.46	—0.094	—0.096	—0.82	—0.50†	0.060	0.014*	—0.031	—0.005†	—0.86	—0.46§	6.70	6.41
SE of difference	± 0.105		± 0.0188		± 0.105		± 0.0079		± 0.0087		± 0.179		± 0.224	

of these experiments differed only slightly from treatment to treatment. In the second experiment, necrotic symptoms first appeared in the low-calcium and low-nitrogen treatments, and at harvest the low-phosphorus treatments were still symptomless. The results of these two experiments were found to support those of the main factorial experiment, in that the effect of nickel in reducing yield and producing necrosis was found to follow the same pattern.

DISCUSSION

The results in the foregoing tables show that nickel very significantly depressed yield of dry matter and the uptake of the major nutrients with the exception of calcium, where uptake was increased. Vergnano¹¹), using fresh-tissue extracts of oat stems, found that nickel reduced nitrate content and caused accumulation of phosphate.

The increased uptake of calcium by plants receiving nickel had been noted before when fresh-tissue extracts were being used as a measure of nutrient status. At the time no particular importance was attached to this result because of the possibility that rate of extraction of calcium from nickel-toxic tissue differed from that for normal tissue. Ash analysis has given the same results, which means that a toxic trace element is affecting the uptake of a major element. While it is difficult to advance a possible explanation for this phenomenon, its results are in keeping with the observed effect of calcium on toxicity symptoms. Calcium (of the cations) is found to be the most active in reducing the toxic symptoms produced by nickel and this suggests that the two effects are related. It is interesting to note that the smaller reductions brought about by increased magnesium or potassium supply are not accompanied by increased uptakes of these elements. Divalent cations would be expected to modify the absorption of nickel more than monovalent cations and this is found experimentally. It appears, however, that the calcium effect derives a second impetus as a result of its increased uptake in the presence of nickel.

The reduction in uptake of other elements is more in keeping with the observed toxic action of nickel on roots, which become stunted and brown in colour with suppression of secondary root development. In experiments dealing with the absorption and translocation of iron

by nickel-toxic roots, C r o o k e ³⁾, has found that only a small and constant amount of the iron absorbed is translocated.

The effect of the various treatments in reducing or increasing toxicity symptoms is not reflected in the uptake of nickel. When treatment differences are eliminated no correlation is found between symptoms and nickel level in the plant. In a paper dealing with iron-nickel relations, C r o o k e, H u n t e r and V e r g n a n o ⁴⁾, have pointed out that good correlation with symptoms is obtained if the Ni/Fe ratio in the plant is used instead of the Ni or Fe content of the plant. When this procedure was applied to the present results, only a small correlation was found due to the fact that treatment is affecting symptoms and the ratio in a like manner. When the effect of treatment is removed statistically the correlation between symptoms and the Ni/Fe ratio is not significant. This does not mean that the ratio approach is necessarily incorrect but rather that this experiment is not capable of — and indeed was not designed with a view to — investigating the relationship between the two. In the case of symptoms of more than moderate severity, a graph of symptoms versus Ni/Fe ratio suggests that a definite relationship exists. For mild symptoms, the wide range of ratios which have been produced as the result of treatment differences make demonstration of the correlation difficult. Unpublished results (C r o o k e ³⁾) of water-culture experiments in which nickel and iron level in the substrate have been varied over wide limits show a convincing positive correlation between degree of symptoms and the Ni/Fe ratio in the plant.

These experiments while confirming earlier sand culture results ^{11) 12)}, agree also with the results observed in the field following the application of fertilizers to these nickel-toxic soils. This raises the question of applicability of these sand-culture results to explain field observations. If we consider the two main effects viz. the beneficial effect of increased calcium supply and the adverse effect of a high phosphorus supply, it seems reasonable to assume that the latter effect, since it probably occurs within the plant, operates in the same way under both sets of conditions.

The application of calcium to a soil produces other effects, notably change in soil pH, besides increasing the level of calcium in the soil. H u n t e r and V e r g n a n o ⁸⁾, have shown that calcium sulphate had not the beneficial effect of calcium carbonate, which suggested that the effect was due to a reduction in available nickel following

change in soil pH. This contention has been further borne out in a series of pot experiments (C r o o k e ³⁾) involving liming studies using CaCO_3 or Na_2CO_3 , carried out in conjunction with laboratory experiments to examine the effect of change in soil pH on the recovery of nickel from a soil. It is found that increase in pH is accompanied by a decrease in exchangeable nickel and this effect can be produced either by Ca^{++} or Na^+ .

In sand culture, however, the position is quite different since no pH change is involved following the increased supply of calcium in the nutrient solution, and furthermore the "available" nickel level in the nutrient solution is unaffected by changes in its cation content. One reason for the reduction in toxic symptoms could be a reduction in the uptake of nickel because of the increased cation content of the nutrient solution. The divalent cations Ca^{++} and Mg^{++} , would be expected to exert a relatively greater beneficial effect than K^+ and this is found here. The uptake of nickel, however, is not significantly reduced by increases in any of these cations although this does not rule out the possibility that the rate of absorption of nickel was not reduced under these conditions.

The phosphorus-nickel relationship can probably best be explained in terms of their separate effects on iron metabolism. C r o o k e *et al.* ⁴⁾ have shown that a high level supply of iron will prevent the appearance of nickel toxicity symptoms in oat plants. Increase in phosphorus supply in the presence of a fixed iron supply would be expected to reduce the uptake and translocation of iron, and this in turn would increase the Ni/Fe ratio in the plant and so produce an increase in toxicity symptoms. This is the simplest explanation and further experiments are required to test this hypothesis.

The interaction between phosphorus and another heavy metal, cobalt, has been the subject of a recent paper by N i c h o l a s and T h o m a s ¹⁰⁾. Using tomato grown in soil culture they found that the toxic symptoms produced by the addition of cobalt were alleviated on increasing the phosphorus supply. The paper records no data on the availability and uptake of the added cobalt following the additions of fertilizer phosphorus. A priori, the results suggest that an increase in phosphorus supply decreased the level of cobalt available to the plants. In contrast to this, A s k e w and D i x o n ²⁾ have found that uptake of cobalt was increased following the addition of phosphorus as superphosphate. Their experiments, carried out

in soil culture, investigated the effect of lime and superphosphate additions on the uptake of added cobalt by various pasture plants. Lime was found to depress uptake of cobalt.

Hunter and Vergnano⁹⁾ have examined the effects of various heavy metals on oat plants and concluded that nickel and cobalt behave very similarly in their toxic action, the main difference being one of degree — cobalt being less active than nickel. In view of the above findings the authors thought it worthwhile to repeat the relevant treatments in the main factorial experiment involving low and high phosphorus, but to supply cobalt in the nutrient solution at 5 and 20 ppm to oats in sand culture.

TABLE VI

	Yield of dr.m.(g)	% P	Ppm		Total uptake			Symptoms *)	
			Co	Fe	P(g)	Co (mg)	Fe(mg)	Necr.	Chl.
<i>Normal P</i>									
Control	10.65	0.66	— §)	65	0.07	—	0.69	O	O
+ 5 ppm Co	9.18	0.72	162	59	0.07	1.48	0.54	O	M
+ 20 ppm Co	5.38	1.25	1075	45	0.07	5.78	0.24	M	H
<i>High P</i>									
Control	13.41	1.29	—	63	0.17	—	0.84	O	O
+ 5 ppm Co	7.94	2.57	176	54	0.20	1.39	0.42	O	M+
+ 20 ppm Co	5.13	2.49	955	41	0.13	4.90	0.21	M	H

*) on scale high (H), medium (M); low (L.).

§) not determined.

The experiment was carried out in a greenhouse using artificial illumination (daylight fluorescent tubes). 5 ppm cobalt produced a prominent interveinal chlorosis in the oat plants at both rates of phosphorus supply. Plants receiving 20 ppm cobalt had necrotic leaf margins and tips in addition to being severely chlorotic. The appearance of the plants changed also; leaves were narrow and the habit became spiky. The increase in symptoms resulting from an increase in phosphorus supply was not so definite as was obtained with nickel. Chlorotic symptoms at 5 ppm cobalt level definitely increased in severity on increasing the phosphorus supply, but at the higher cobalt level no change in symptoms was seen. From Table VI it will be seen that cobalt (at both levels) produced a greater reduction in yield of dry matter (per treatment of 3 pots) when high phosphorus was supplied. Uptake of cobalt was not markedly

affected by rate of phosphorus supply, while iron uptake was reduced with increasing cobalt in the substrate.

While certain of the results of this experiment are not so clear-cut as those found for nickel, there are features common to both sets of data which support the conclusions drawn about the similarity between nickel and cobalt toxicity. The results of Askew and Dixon, in so far as they are directly comparable, are in agreement with those reported here in that they show that the interaction between the metal and phosphorus is operating in the same direction viz. in increasing the uptake of the metal and in aggravating the toxic symptoms produced. Minor variations in degree, but not in kind, are to be expected when different plant species and experimental conditions are involved, but it is not clear why Nicholas and Thomas found the interaction to operate in the reverse direction for tomato in soil culture. The inference must be that a dependent variable factor was modified by the conditions of experiment. The high pH (6.5) of the soil used, together with the addition of cobalt in solution to soils which had received the heavy differential superphosphate dressings employed, suggests that precipitation of cobaltous phosphate took place ^{1) 14)}, or that positional availability of cobalt was operative.

Because of the wide differences between the experiments discussed here, it is impossible to attempt an explanation of the conflicting results obtained. These apparent discrepancies in no way invalidate the findings, which hold true for a particular set of experimental conditions, but they do serve to draw attention to the complex nature of the problem under investigation, and to stress that results obtained under a particular set of conditions can seldom be used to predict precisely behaviour under another set of conditions, or to proceed further to the derivation of a general relationship.

SUMMARY

1. A factorial sand-culture experiment has been utilized to investigate the effect of variation in the level of supply of major nutrients on nickel toxicity in oat plants. Two levels of each of the nutrients, nitrogen, phosphorus, potassium, calcium and magnesium were used in conjunction with two levels of nickel in the nutrient solution (0 and 2.5 ppm).

2. The yield of dry matter is markedly reduced by nickel, the effect being greatest when calcium or potassium supply is low or phosphorus supply is

high. Yield can be improved by increasing the first two factors or reducing the third.

3. Symptoms of nickel toxicity in oat plants are briefly described, and it is found that an increase in the rate of supply of nitrogen, potassium, calcium, or magnesium decreases the toxic symptoms while an increase in phosphorus supply has the reverse effect.

4. Uptake of nickel by the plants is not correlated with level of symptoms found. Similarly, use of the Ni/Fe ratio in the plant, which has previously been shown to give a measure of toxicity is found to be of limited applicability in this case. The correlation between symptoms and the Ni/Fe ratio is not statistically significant when treatment differences are removed.

5. An increase in rate of supply of phosphorus causes a significant increase in the uptake of nickel. Variation in the supply of the other major nutrients does not significantly affect uptake of nickel.

6. The pattern of behaviour between nickel and major nutrients found here for sand-cultured oats agrees well with results observed in the field. The inherent danger in generalising about such results and using them to explain plant-soil relationships is commented upon, but it is pointed out that, provided interpretation is not pushed too far, the results obtained here are valid and demonstrate the magnitude and direction of the main effects encountered in the field.

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BIOLOGICAL TRANSFORMATIONS OF PHOSPHORUS IN SOIL

I. THEORY AND METHODS *)

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INTRODUCTION

Synthesis and mineralization of organic phosphorus both occur continuously in moist soils over a wide temperature range. If none of the organic phosphorus synthesized during incubation is subsequently mineralized, and *vice versa*, the amounts of synthesized and mineralized organic phosphorus present in the soil after incubation will represent total synthesis and total mineralization. It is probable, however, that after any finite incubation period, the amounts of synthesized and mineralized organic phosphorus in the soil will be less than total synthesis and total mineralization since some of the phosphorus involved in the transformations will have oscillated between the organic and inorganic forms several times during incubation. The difference between the organic phosphorus content of a soil before and after incubation is thus the difference between total synthesis and total mineralization; it is also the difference between the amounts of synthesized and mineralized organic phosphorus present in the soil after incubation.

Until P^{32} became available, only the difference between the organic phosphorus content of a soil before and after incubation

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could be measured. By means of P^{32} , however, it has been possible to estimate the amount of synthesized organic phosphorus present in the soil after incubation under a wide variety of conditions.

The measurements have been made possible by the isotopic dilution technique for analysis ⁵⁾ and the availability concept developed by Fried and Dean ³⁾. If the change in the organic phosphorus content of the soil is measured at the same time, the amount of mineralized organic phosphorus present after incubation can be estimated also. Furthermore, the relative availability of soil phosphorus and non-radioactive inorganic fertilizer phosphorus to soil organisms can be estimated and expressed in terms of the standard source of inorganic phosphorus containing P^{32} that is added to the soil prior to incubation.

THEORY

In soil to which a standard source of inorganic phosphorus containing P^{32} has been added prior to incubation, synthesized organic phosphorus present after incubation will be derived from this source and from inorganic soil phosphorus. The general relation between the two sources of inorganic phosphorus and the amounts of synthesized organic phosphorus present after incubation is shown in equation (1)

$$\frac{I_a}{I_b} = \frac{O_a}{O_b} \quad (1)$$

where I_b is the quantity of inorganic phosphorus containing P^{32} added to the soil, and I_a is arbitrarily designated as the amount of available soil phosphorus. A unit of I_a is equivalent in availability to a unit of inorganic phosphorus containing P^{32} after the latter is added to the soil. O_b is the amount of synthesized organic phosphorus derived from inorganic phosphorus containing P^{32} , and O_a is the amount of synthesized organic phosphorus derived from inorganic soil phosphorus. I_a includes both the amount of phosphorus available from the native soil inorganic phosphorus and the amount available from the inorganic phosphorus formed by mineralization of soil organic phosphorus. Equation (1) is applicable irrespective of any reactions that the P^{32} atoms may undergo in the soil, since for any given initial specific activity of the added inorganic phosphorus, every P^{32} atom added to the soil will on

the average be accompanied in all its reactions by a constant number of P^{31} atoms derived from the added inorganic phosphorus.

I_b is known, and O_b can be determined from the specific activity of the organic phosphorus in the soil after incubation and the initial specific activity of the inorganic phosphorus added to the soil. Since O_a cannot be measured, I_a cannot be calculated from equation (1). Nevertheless, I_a can be calculated if it can be assumed (a) that under constant environmental conditions the total amount of synthesized organic phosphorus present after incubation is constant irrespective of the quantity of inorganic phosphorus containing P^{32} added to the soil, (b) that the proportion of the added inorganic phosphorus that is available for organic phosphorus synthesis by the soil organisms is constant for different rates of application, and (c) that the amount of soil phosphorus available to the soil organisms (I_a) is independent of the rate of application of inorganic phosphorus containing P^{32} .

When the soil is unamended except for inorganic phosphate applications, the supply of phosphorus generally will not limit the intensity of microbial activity; hence, the first assumption may be considered reasonable. In support of the remaining two assumptions, Fried and Dean³⁾ found that when dry, powdered, monobasic calcium phosphate containing P^{32} was uniformly mixed with soil, and the uptake of P^{32} from the soil by oats was measured, the calculated amount of available soil phosphorus was reasonably constant for the different quantities of monobasic calcium phosphate added.

Granting these assumptions, the following equations may be derived.

$$O_a = O_s - O_b \quad (2)$$

O_s is the total amount of synthesized organic phosphorus present in soil after incubation and is assumed constant for a soil under specified environmental conditions but with differing amounts of inorganic phosphorus containing P^{32} added to the soil. When $O_s - O_b$ is substituted for O_a in equation (1), on solving for O_s the following equation is obtained.

$$O_s = \frac{O_b I_a}{I_b} + O_b \quad (3)$$

Assuming that two rates of inorganic phosphorus I_a' and I_b''

are added to the soil, and that O_b' and O_b'' amounts of synthesized organic phosphorus are present after incubation, the two expressions each equal to O_s may be equated as shown below.

$$\frac{O_b' I_a}{I_b'} + O_b' = \frac{O_b'' I_a}{I_b''} + O_b'' \quad (4)$$

Solving for I_a , equation (5) is obtained.

$$I_a = \frac{O_b'' - O_b'}{O_b' - O_b''} \frac{I_b' - I_b''}{I_b'} \quad (5)$$

Since I_b' and I_b'' are known, and O_b' and O_b'' can be determined, I_a can be calculated. By appropriate substitution of numerical values for I_a , I_b , and O_b in equation (3), O_s can also be calculated.

If the total organic phosphorus in the soil before incubation is equal to the total organic phosphorus present after incubation, then O_s will equal O_m , where O_m is the total amount of soil organic phosphorus mineralized during incubation. If there is a change in total soil organic phosphorus during incubation,

$$O_m = O_s \pm D \quad (6)$$

where D is the difference between total organic phosphorus in the soil before and after incubation.

Once O_s has been found, it is possible to determine the availability of nonradioactive inorganic phosphorus fertilizers added to the soil. The radioactive and nonradioactive forms of phosphorus are added to the soil at the same time, and the soil is incubated under the same environmental conditions as were originally employed for obtaining O_s . After incubation, O_s can be expressed as follows:

$$O_s = O_{af} + O_{bf} + O_{cf} \quad (7)$$

where O_{af} , O_{bf} , and O_{cf} are the amounts of synthesized organic phosphorus derived from the soil phosphorus, the inorganic phosphorus containing P^{32} , and the nonradioactive inorganic phosphorus fertilizer, respectively. Equation (7) may be rearranged as shown below.

$$O_s - O_{bf} = O_{af} + O_{cf} \quad (8)$$

If equation (7) is now modified to include the presence of non-

radioactive inorganic fertilizer phosphorus in the soil, the following expression is obtained:

$$\frac{I_a + I_c}{I_b} = \frac{O_{af} + O_{cf}}{O_{bf}} \quad (9)$$

where I is the availability of the nonradioactive fertilizer in units of the added inorganic phosphorus containing P^{32} . Substituting $O_s - O_{bf}$ for $O_{af} + O_{cf}$ in equation (9), equation (10) is obtained.

$$\frac{I_a + I_c}{I_b} = \frac{O_s - O_{bf}}{O_{bf}} \quad (10)$$

Solving for I_c equation (11) is obtained.

$$I_c = \frac{I_b(O_s - O_{bf})}{O_{bf}} - I_a \quad (11)$$

Since I_a , I_b , and O_s are known, and O_{bf} can be determined, I_c can be calculated. In this manner, the relative availability of nonradioactive inorganic phosphorus fertilizers to soil organisms can be estimated.

METHODS

Extraction and determination of organic P^{31} and P^{32} in soil

To obtain the data required in the theoretical development, samples of soil (usually 10 g) that had been incubated with P^{32} were analyzed for organic P^{31} and P^{32} by the following procedure. The soil sample was treated with 25 ml of N HCl, and the mixture was warmed on a hot plate at about $70^\circ C$ for 5 minutes. The mixture was filtered into a 250 ml volumetric flask, the filter paper and soil were washed with 100 ml of N HCl, and the acid extract was made to volume.

The soil and filter paper were placed in a 250 ml erlenmeyer flask and extracted with 200 ml of 0.5 N NaOH for 16 hours at $23-27^\circ C$. The alkaline extract was filtered into a 500 ml erlenmeyer flask. The soil and filter paper were returned to the 250 ml erlenmeyer flask and extracted with 200 ml of 0.5 N NaOH at $85-90^\circ C$ for 16 hours, the flask being fitted with a bunsen valve to minimize loss of water. The second NaOH extract was cooled to $23-27^\circ C$ and added to the first NaOH extract. The combined extracts were diluted to 500 ml with water, and mixed. After mixing, the suspended material was allowed to settle at the bottom of the flask. To determine total phosphorus, aliquots of the clear HCl and

NaOH extracts were combined and digested on a hot plate with 1 or 2 ml of 70 percent perchloric acid. Inorganic phosphorus in the resulting solution was determined by the method of Dickman and Bray¹⁾. Inorganic phosphorus in undigested combined aliquots of the HCl and NaOH extracts also was determined by the method of Dickman and Bray¹⁾ using the technique of Dyer and Wrenshall²⁾ for colored extracts. Organic phosphorus was calculated by difference.

To determine organic P³², 100 ml of the clear NaOH extract was transferred to a 125 ml erlenmeyer flask containing 8 ml of 12 *N* HCl and about 250 mg of activated charcoal. The ingredients were mixed on a wrist-action shaker for 1 hour. Similar second and third additions of charcoal were made, and the ingredients were mixed for two additional 1-hour periods. The mixture was then filtered, and the filter paper and charcoal were washed with 60 ml of 0.5 *N* HCl. By this process, the organic phosphorus originally present in the NaOH extract was adsorbed and remained adsorbed on the activated charcoal. The inorganic phosphorus in the mixture was adsorbed by the charcoal to only a minor extent.

The filter paper and charcoal were transferred to a 50 ml pyrex beaker, treated with 10 ml of *N* NH₄OH and 1 ml of 10 percent Mg(NO₃)₂, evaporated to dryness on a hot plate, and ignited at 500–550°C for 16 hours. The residue was treated with 1 ml of concentrated HCl, warmed for 1 minute at about 70°C on a hot plate, diluted with 20 ml of water, and warmed for 30 minutes at about 70°C on a hot plate. The solution obtained was then filtered into a 50 ml volumetric flask, the filter paper was washed with water, and the filtrate was made to volume. Inorganic phosphorus in the filtrate was determined by the method of Dickman and Bray¹⁾.

A jacketed, thin-walled, solution-counter tube in conjunction with an electronic scaler was used to measure the radiation emitted from the P³² in the filtrate. Radiation from the total soil organic P³² was then calculated from the relationship

$$\text{Radiation from total soil organic P}^{32} = \frac{\text{Total organic P}^{31} \text{ plus P}^{32} \text{ in soil}}{\text{Organic P}^{31} \text{ plus P}^{32} \text{ in filtrate used for measurement}} \times \frac{\text{Radiation from P}^{32} \text{ in filtrate used for measurement}}{\text{used for measurement}}$$

The amount of synthesized organic phosphorus derived from the inorganic phosphorus containing P^{32} could then be calculated from the relationship

$$\frac{\text{Synthesized organic phosphorus derived from inorganic phosphorus containing } P^{32}}{\text{Radiation from total soil organic } P^{32}} = \frac{\text{Radiation from added inorganic } P^{32}}{\text{Quantity of inorganic phosphorus containing } P^{32} \text{ added to the soil}} \times$$

where the total solution volume was the same for the P^{32} measurements on soil organic phosphorus and added inorganic phosphorus. Total synthesized organic phosphorus and soil phosphorus available to soil organisms were calculated in the manner outlined in the preceding section.

Comments

In these studies, separated P^{32} in the form of H_3PO_4 was dissolved in water together with KH_2PO_4 , and the mixture was used as a standard source of inorganic phosphorus containing P^{32} . To avoid significant radiation damage to the soil microorganisms, specific activities less than 0.05 mc of P^{32} mg of P^{31} plus P^{32} were employed ⁴).

The extraction procedure used in these studies was similar to the procedure recently developed by Mehra, *et al.* ⁶), and, like the latter, was found to extract more organic phosphorus from soils than the method described by Pearson ⁷).

Digestion of the combined HCl and NaOH extracts in perchloric acid for total phosphorus determinations was satisfactory, provided the digest was neutralized with NH_4OH prior to addition of the molybdate reagent. When ferric iron interfered with color development, its effect was eliminated by employing larger quantities of $SnCl_2$ ^{*}).

Quantitative separation of organic from inorganic phosphorus was necessary for the determination of organic P^{32} . Only the combined NaOH extracts were employed for this separation. The HCl extract was not used because (1) it contained less than 5 percent of the soil organic phosphorus, (2) the specific activity of the

^{*}) Legg, J. O., Unpublished data, U.S. Department of Agriculture and Iowa Agricultural Experiment Station.

organic phosphorus it did contain was similar to the specific activity of the organic phosphorus in the combined NaOH extracts, and (3) it contained approximately 60–80 percent of the inorganic P^{32} .

Activated charcoal (U.S.P. powder) manufactured by Merck and Co., Rahway, N.J., was used for adsorbing the organic phosphorus. Before use, the material was thoroughly washed with *N* HCl to remove traces of inorganic phosphorus. When employed in the specified manner, the charcoal adsorbed from 85–90 percent of the organic phosphorus and less than 1 percent of the inorganic phosphorus in the acidified NaOH solution. In making calculations, it was assumed that the adsorbed organic phosphorus was representative of the total soil organic phosphorus. The error in organic P^{32} determinations caused by adsorption of inorganic phosphorus by the charcoal was estimated by adding various quantities of radioactive inorganic phosphorus to soils, extracting the soils within 15 minutes by the method previously described, and determining the apparent quantities of organic P^{32} formed. An average of 0.2 ± 0.08 percent of the inorganic phosphorus added appeared to have been converted to organic phosphorus. Suitable allowance was made for this analytical error.

It was assumed in these investigations that isotopic exchange between inorganic and organic phosphorus does not occur⁵). This assumption was investigated by sterilizing samples of soil in an autoclave, and then incubating them under sterile conditions with inorganic phosphorus containing P^{32} . In no instance did any apparent synthesis of organic P^{32} occur.

SUMMARY

Mathematical expressions were developed for calculating (1) the availability of soil phosphorus and nonradioactive inorganic fertilizer phosphorus to soil organisms, the measurements being expressed in terms of a standard source of inorganic phosphorus containing P^{32} added to the soil prior to incubation, and (2) the amounts of synthesized and mineralized organic phosphorus present in soils after incubation. Analytical procedures for obtaining the necessary data were described.

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BIOLOGICAL TRANSFORMATIONS OF PHOSPHORUS IN SOIL

II. FACTORS AFFECTING SYNTHESIS OF ORGANIC PHOSPHORUS *)

by C. A. I. GORING **)

INTRODUCTION

The continuous interchange of organic and inorganic forms of phosphorus in soil is a process of considerable interest, not only because it may influence the phosphorus nutrition of plants but also because it is in itself a vital part of soil biology. The process may be affected by many physical, chemical and biological factors. For example, if readily available carbohydrates together with inorganic nitrogen and inorganic phosphorus are added to soils, synthesis may exceed mineralization of organic phosphorus. The reverse is usually true when samples of field soils are incubated without these amendments.

Until P^{32} became available, measurement of the change in organic phosphorus content of a soil during incubation was the principal method for estimating the extent of biological phosphorus transformations in soil. In a previous paper ³⁾, the author described a method employing P^{32} by which the amounts of synthesized and mineralized organic phosphorus present in a soil after incubation could be measured. In the present investigation this method was used in an effort to gain a better understanding of the nature and extent of biological soil phosphorus transformations. Preliminary studies

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were made of some of the effects of moisture content, time, temperature, pH, and soil composition on synthesis of organic phosphorus in a variety of soils.

MATERIALS AND METHODS

The soil samples were air dried, crushed, sieved through a 20-mesh sieve, and thoroughly mixed prior to use. Total organic phosphorus, and synthesized organic phosphorus were determined by the methods previously described³). Total soil phosphorus was determined by digestion of soil samples in perchloric acid and colorimetric estimation of inorganic phosphorus by the method of Dickman and Bray²). Total inorganic phosphorus was obtained by difference. Total nitrogen was determined by the Kjeldahl method¹) and total carbon was determined by the dry combustion method¹). The total carbon was presumed to be entirely in the organic form, since the soil samples were noncalcareous. The pH measurements were made on 1 to 2.5 soil to water suspensions using a glass electrode assembly. All analytical data are expressed on the basis of air-dry soil. The location, type, pH, and phosphorus, nitrogen, and carbon contents of the various samples are given in Table I.

Except for the variations in experimental details listed below for the individual experiments, the following general incubation procedure was employed. Ten-g soil samples were placed in 2-ounce, screw-cap bottles. Phosphorus was added in water solution at rates of 10 and 75 ppm of phosphorus as KH_2PO_4 tagged with P^{32} , and the soils were incubated for 1 week at 25°C prior to analysis. The soil samples were intermittently aerated by removal of the bottle caps and exposure of the samples to the air.

Synthesis of organic phosphorus as affected by length of incubation period was determined by placing the soil samples in carbon filter tubes, moistening with 35 percent water, and incubating for $\frac{1}{4}$, 1, 5, 14, and 28 days. Air saturated with water vapor was forced through the samples continuously.

In determining the effect of temperature, the soil samples and the water solutions of KH_2PO_4 were preheated or precooled to the desired temperatures prior to mixing. Thirty percent water was added to soil F 1516, and 35 percent water was added to soil F 1518.

All incubation temperatures varied no more than $\pm 2^{\circ}\text{C}$ from the stated values.

TABLE I

Location, type, pH, and phosphorus, nitrogen, and carbon contents of the soil samples employed									
Soil sample no. *)		Location	Soil type	pH	Total or- ganic P	Total inor- ganic P	Total N	Total or- ganic C	
Iowa	U.S.D.A.				x_5	x_1	x_2	x_3	x_4
					ppm	ppm	ppm	ppm	ppm
F 729		Iowa	Grundy silt loam	6.9	366	514	3460	40,1	
F 734		Iowa	Haig silty clay loam	6.1	368	232	2150	26,5	
F 735		Iowa	Edina silt loam	6.6	457	281	3850	50,0	
F 738		Iowa	Seymour silt loam	5.4	323	213	2220	26,1	
F 740		Iowa	Hayden fine sandy loam	6.4	130	170	1390	10,8	
F 743		Iowa	Muscataine silt loam	5.5	490	312	3200	37,1	
F 750		Iowa	Garwin silt loam	6.3	296	316	3250	35,6	
F 767		Texas	Wilson silty clay loam	6.3	102	104	1840	23,3	
F 769		Texas	Houston silty clay	7.4	190	500	3560		
F 770		Texas	Houston silty clay	7.3	70	135	1350	27,4	
F 773		Colorado	(Unknown) fine sandy loam	6.4	155	421	1790	18,4	
F 1515		Iowa	Thurman fine sand	5.4	109	157	670	7,5	
F 1516		Iowa	Clarion fine sandy loam	7.2	153	204	1520	17,3	
F 1517		Iowa	Clarion loam	5.7	185	176	1240	14,5	
F 1518		Iowa	Webster silt loam	6.1	228	175	2180	28,7	
F 1519		Iowa	Wabash silty clay	6.3	227	243	2260	28,4	
F 1520		Iowa	Seymour silt loam	5.5	290	272	1950	22,1	
	47867	North Dakota	Cheyenne fine sandy loam	7.2	125	483	1520	16,7	
	E 787	Virginia	Davidson clay loam	6.0	180	587	1400	20,2	
	45643	Louisiana	Ruston fine sandy loam	5.9	24	86	280	5,5	
	51119	Illinois	Brookston silty clay loam	6.3	527	594	2910	32,0	
	51112	Maryland	Hagerstown silt loam	5.9	272	382	2320	25,4	
	47871	North Dakota	Cheyenne fine sandy loam	7.1	112	405	1200	13,8	
	46264	Mississippi	Sharkey clay	6.0	125	966	1780	18,4	
F 1528	51631	North Dakota	Edgeley silt loam	5.6	251	233	2040	23,1	
F 1530	51629	North Dakota	Fargo clay	5.9	338	306	2770	39,0	
F 1532	51630	North Dakota	Langdon loam	6.5	294	234	2870	29,8	
F 1534	51626	South Dakota	Barnes loam	6.2	281	323	1950	23,6	
F 1536	51625	South Dakota	Kranzburg silt loam	5.9	403	273	2710	30,7	
F 1538	51624	South Dakota	Moody silt loam	6.0	450	302	2680	30,0	
F 1540	51589	Nebraska	Moody silt loam	6.3	133	363	1000	10,1	
F 1542	51587	Nebraska	Hastings silt loam	5.3	191	285	1620	18,6	
F 1544	51588	Nebraska	Carrington clay loam	6.0	114	182	1160	11,5	
F 1546	51616	Minnesota	Waukegan silt loam	5.5	266	470	1810	24,0	
F 1548	51618	Minnesota	(Unknown) silt loam	6.6	323	281	1820	20,2	
F 1550	51619	Minnesota	Barnes silt loam	6.2	468	300	3290	36,3	
F 1556	51620	Iowa	Carrington loam	5.5	561	263	3320	37,4	
F 1558	51580	Wisconsin	Miami silt loam	6.5	133	255	1160	12,2	
F 1560	51627	Michigan	Fox sandy loam	6.3	152	344	900	11,0	
F 1562	51628	Michigan	Miami loam	6.4	170	212	870	13,3	
F 1564	51622	Illinois	Muscataine silt loam	4.9	310	190	1700	19,2	
F 1566	51623	Illinois	Elliot silt loam	4.7	305	171	2030	24,4	

*) Samples of the soils with both Iowa and U.S.D.A. numbers are located at the Agronomy Department, Iowa State College, Ames, Iowa, and the Soils Division, Plant Industry Station, B.P.I.S.A. Beltsville, Maryland. Nitrogen and pH determinations were made on the samples located at Beltsville and phosphorus and carbon determinations were made on the samples located at Ames. All of the remaining soils were analyzed at Ames.

Changes in pH were produced by adding HCl or NaOH to the soils prior to incubation with P^{32} . Thirty percent water was added to soils F 740, F 743, F 750, and F 1520, and 35 percent water was added to soils F 1519 and F 769.

The effect of moisture content on synthesis of organic phosphorus was determined by spreading the soil samples in petri plates, moistening with 30, 40, 50, and 60 percent water containing tagged phosphorus, and incubating for 1 and 7 days. The initial moisture contents were maintained throughout the incubation periods.

For the soils incubated without P^{32} prior to being dried and then incubated with P^{32} , 50-g samples in 125-ml Erlenmeyer flasks were initially moistened with 30 percent water. These samples were maintained at 25, 45, and 65°C for 1 week and then air dried. Three-ml aliquots of water containing enough tagged phosphorus to supply 20 and 100 ppm of inorganic phosphorus on the soil basis were added to 10-g subsamples of the soils, which were then incubated at 25°C for 1 week.

The effect of wetting and drying of the soils on synthesis of organic phosphorus was determined by distributing the soil samples in small petri plates, moistening them initially with 30 percent water, and incubating them at 25°C. Half of the soil samples were maintained at this moisture content for 3 weeks. The remaining samples were air dried and remoistened every fourth day of the 3-week incubation period.

The soil samples employed for determining the effect of freezing and thawing on synthesis of organic phosphorus were moistened with 30 percent water. Half of the soil samples were maintained at 25°C for 30 days. The remaining samples were frozen for a 16-hour period every fifth day of the 30-day incubation period.

The relation of organic carbon, total nitrogen, total inorganic phosphorus, total organic phosphorus, and pH to synthesis of organic phosphorus was investigated for (1) 41 soils incubated with P^{32} , and (2) 22 soils incubated without P^{32} prior to air drying and then incubated with P^{32} . For the former soils, 10 and 75 ppm of inorganic phosphorus containing P^{32} was added to 10-g soil samples prior to incubation in the usual manner. The moisture levels used were optimum for the different types of soils. In the latter procedure, 40-g soil samples were incubated in open glass dishes for 1 week and then air dried. Eight-g subsamples to which 12.5 and 94 ppm

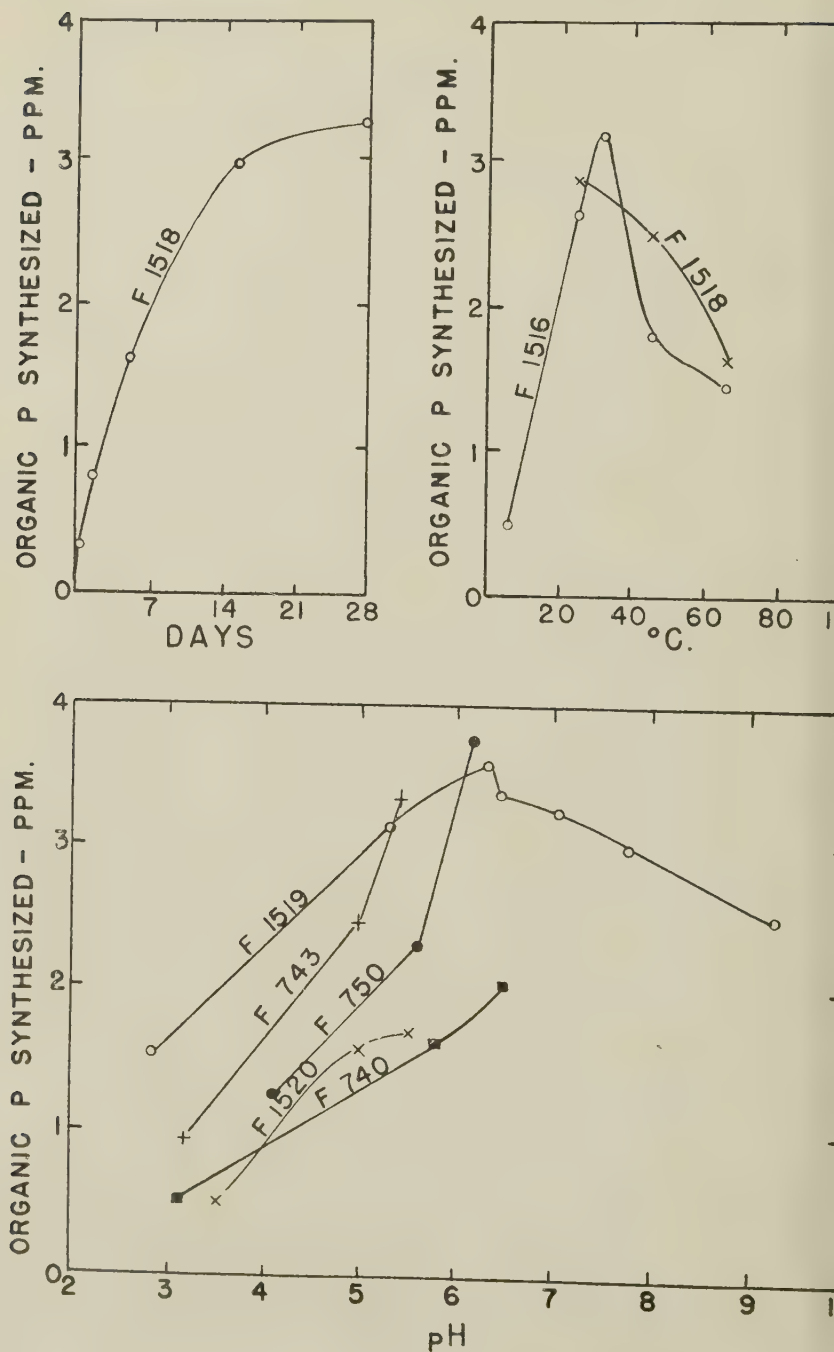


Fig. 1. Effect of incubation period, temperature, and pH on synthesis of organic phosphorus in soils.

of phosphorus as KH_2PO_4 tagged with P^{32} had been added were then incubated for 1 week.

RESULTS

The effect of incubation period, temperature, and pH on synthesis of organic phosphorus are shown in Figure 1. The rate of synthesis of organic phosphorus in soil F 1518 decreased very rapidly with increasing length of the incubation period. The average rate of synthesis for the first 14 days of incubation was 0.21 ppm of phosphorus per day, and for the period from 14 to 28 days it was 0.024 ppm of phosphorus per day.

On incubation at different temperatures, maximum synthesis in soil F 1516 occurred between 25 and 45°C. Some synthesis occurred at as low a temperature as 7°C. In soil F 1518, synthesis at 25°C was greater than at 45 or 65°C. It is probable that in this soil also maximum synthesis occurred between 25 and 45°C.

The data showing the effect of pH on synthesis of organic phosphorus in the five soils studied indicate that the optimum pH for synthesis is greater than 5.5, and the results for soil F 1519 suggest that the optimum pH lies between 5.5 and 7.5.

TABLE II

Synthesis of organic phosphorus in soils incubated at different moisture contents			
Soil	Incubation period	Water added	Total synthesized organic P present after incubation
	days	per cent	ppm
F 1516	1	30	1.87
		40	2.07
		50	1.83
		60	2.07
	7	30	3.27
		40	2.99
		50	3.01
		60	3.23
F 1517	1	30	1.21
		40	1.49
		50	1.55
		60	1.61
	7	30	2.79
		40	2.85
		50	2.59
		60	2.85

Table II illustrates the effect of moisture content of the soil on synthesis of organic phosphorus. Within the moisture range employed, differences in soil moisture content appeared to have little or no effect on synthesis of organic phosphorus.

Table III shows synthesis of organic phosphorus in soil samples pre-incubated at different temperatures, air dried, and then incubated at 25°C with inorganic phosphorus tagged with P^{32} . Pre-incubation temperature had no appreciable effect on synthesis in soil F 1516. In soil F 1517, synthesis after incubation at 65°C appeared to be somewhat less than synthesis after incubation at 25 or 45°C.

TABLE III

Synthesis of organic phosphorus in soils pre-incubated at different temperatures without P^{32} prior to incubation at 25°C with P^{32}		
Soil	Pre-incubation temperature	Total synthesized organic P present after incubation
F 1516	°C	ppm
	25	1.87
	45	1.82
F 1517	65	1.88
	25	1.27
	45	1.19
	65	0.89

Table IV demonstrates the effects of repeated wetting and drying and repeated freezing and thawing of soils on synthesis of organic phosphorus. Both treatments appeared to increase synthesis of organic phosphorus although the magnitude of the effects of freezing and thawing was probably not significant.

Synthesis of organic phosphorus in 41 noncalcareous soils incubated with inorganic phosphorus tagged with P^{32} is shown in Table V. The multiple regression equation expressing the dependence of synthesis (Y) on pH (x_5), organic phosphorus (x_1), inorganic phosphorus (x_2), total nitrogen (x_3), and organic carbon (x_4) was first computed. The multiple correlation coefficient for this regression, 0.457, shows that only a small portion of the variance of synthesis could be accounted for by the independent variables considered, and suggests that some of the independent variables were not of significant value in predicting synthesis.

TABLE IV

Synthesis of organic phosphorus in soils maintained moist, and soils periodically dried and remoistened, and in soils that were not frozen and soils that were periodically frozen during incubation		
Soil	Soil treatment	Total synthesized organic P present after incubation
		ppm
F 1516	Maintained moist	3.20
	Dried and remoistened	4.10
F 1517	Maintained moist	2.80
	Dried and remoistened	4.26
F 1516	Not frozen	4.10
	Periodically frozen	4.28
F 1517	Not frozen	3.03
	Periodically frozen	3.71

TABLE V

Synthesis of organic phosphorus in 41 soils incubated at 25°C for 1 week, and in 22 soils incubated at 25°C for 1 week without P ³² prior to incubation at 25°C for 1 week with P ³²					
Soil	Total synthesized organic P (ppm)		Soil	Total synthesized organic P (ppm)	
	for the incubated samples	for the pre-incubated samples		for the incubated samples	for the pre-incubated samples
	Y	Y'		Y	Y'
F 729	5.53	3.56	47871	1.05	0.64
F 734	2.39	1.39	46264	1.30	1.04
F 735	5.02	3.31	F 1528	1.77	—
F 738	1.70	1.74	F 1530	1.57	—
F 740	2.06	2.11	F 1532	1.99	—
F 743	3.25	1.59	F 1534	3.86	—
F 750	3.56	2.26	F 1536	3.93	—
F 767	5.49	3.32	F 1538	4.31	—
F 770	1.82	0.83	F 1540	6.08	—
F 773	2.97	1.95	F 1542	2.41	—
F 1515	0.98	0.59	F 1544	2.78	—
F 1516	2.64	1.98	F 1546	2.15	—
F 1517	2.37	1.35	F 1548	2.75	—
F 1518	2.80	2.48	F 1550	3.02	—
F 1519	3.57	—	F 1556	3.53	—
F 1520	1.78	1.84	F 1558	1.95	—
47867	1.92	1.11	F 1560	1.78	—
E 787	4.43	2.20	F 1562	2.08	—
45642	0.69	0.78	F 1564	2.49	—
51119	2.94	1.74	F 1566	1.82	—
51112	6.23	3.38			

It was shown in Figure 1 that variation in pH over a wide range influences synthesis of organic phosphorus. Statistical tests demonstrated, however, that in the group of 41 soils employed pH was not significantly correlated with organic phosphorus synthesis. Total inorganic phosphorus also was not significantly correlated with organic phosphorus synthesis.

The regression equation computed after elimination of the two independent variables pH and inorganic phosphorus was significant at the 5 percent level. The multiple correlation coefficient, 0.444, associated with this regression was scarcely different from the coefficient that included all 5 variables.

The individual correlation coefficients (Table VI) between organic phosphorus, total nitrogen, and organic carbon were high and it made little difference whether any or all of these variables were used to predict synthesis. The correlation coefficient, 0.429, for the regression of synthesis on total nitrogen was almost as great as the multiple correlation coefficient, 0.444, obtained using all three independent variables.

TABLE VI

Correlation coefficients between total organic phosphorus, total inorganic phosphorus, total nitrogen, total organic carbon, pH, and total synthesized organic phosphorus present after incubation					
Variables	Correlation coefficients				
	Total inorganic P	Total N	Total organic C	pH	Total synthesized organic P present after incubation
Total organic P	0.106	0.857 **)	0.802 **)	-0.273	0.312 *)
Total inorganic P	—	0.176	0.116	0.149	0.117
Total N	—	—	0.957 **)	-0.0320	0.429 **)
Total organic C	—	—	—	0.0104	0.404 **)
pH	—	—	—	—	0.131

*) Significant at the 5 percent level.

**) Significant at the 1 percent level.

Despite the significant correlations obtained in the foregoing analysis it is obvious that the major portion of the variance in synthesis could not be accounted for by the independent variables considered. This situation might be explained on the basis that the energy states of the soils were not highly correlated with their organic carbon, total nitrogen, and organic phosphorus contents.

If this supposition were true, the correlation might be improved upon decomposition of the more readily-available energy material prior to incubation for measurement of synthesis. Accordingly, samples of 22 soils were pre-incubated for 1 week without P^{32} , and then air dried. After remoistening and incubation for another week with P^{32} , synthesis was measured. Table V shows synthesis of organic phosphorus in these preincubated soils.

Synthesis in the preincubated soils varied from 0.59 to 3.56 ppm of phosphorus as compared to 0.69 to 6.23 in the incubated soils. In almost all instances, synthesis in the incubated soils exceeded synthesis in the preincubated soils, sometimes by as much as 100 percent.

The regression of Y on x_1 , x_3 , and x_4 for the 22 samples incubated directly with P^{32} was significant at the 5 percent level. The multiple correlation coefficient was 0.671. The regression of Y' on x_1 , x_3 , and x_4 for the corresponding pre-incubated samples was significant at the 1 percent level, as was the multiple correlation coefficient 0.713. Preincubation, therefore, increased only slightly the association of synthesis with organic phosphorus, total nitrogen, and organic carbon. The association of synthesis with the three independent variables mentioned above might have been more pronounced if the pre-incubation period had been 2 weeks or longer, but in this instance synthesis occurring after the preincubation period would probably have been relatively small and difficult to measure.

DISCUSSION

The results obtained in this study indicate that synthesis of organic phosphorus, like other biological soil processes, is regulated by a variety of chemical, physical, and biological factors. While the effect of such factors as temperature and time of incubation appeared to be of greater importance than that of moisture, if a wider moisture range had been tested more significant differences in synthesis due to differences in the moisture contents of the soils might have been obtained.

When a number of soil samples were held under constant environmental conditions, a major portion of the variance of synthesis of organic phosphorus was not associated with differences in the

pH or content of organic phosphorus, inorganic phosphorus, total nitrogen, and organic carbon of the soils. Apparently, there are other important factors influencing synthesis of organic phosphorus. Differences in the qualitative and quantitative nature of the soil flora and fauna, and differences in the susceptibility of the soil organic compounds to decomposition are likely possibilities.

The rate of organic phosphorus synthesis was relatively high in some instances. In two samples, it exceeded 6 ppm per week. This exceptional rate of biological phosphorus transformation is probably only temporary, however, and not characteristic of the behaviour over a longer period of time. That such is the case is indicated by the fact that in one soil sample the rate of synthesis decreased rapidly after incubation for 2 weeks (Figure 1). In two other samples, more than half of the organic phosphorus synthesized in a week was synthesized the first day (Table II); and more than half of the organic phosphorus synthesized in 30 days was synthesized the first 7 days (Tables IV and V). It may nevertheless be of significance that high rates of biological phosphorus transformation occur, even if for a short time only, and that such treatments as drying and remoistening increase the rate. The amounts of phosphorus involved are substantial in comparison with those absorbed by crops.

SUMMARY

Synthesis of organic phosphorus in a number of soils incubated under differing environmental conditions was determined. Although the total amount of organic phosphorus synthesized increased with increasing time of incubation, the rate of synthesis decreased. Varying moisture additions from 30 to 60 percent in a loam and a sandy loam did not significantly influence synthesis of organic phosphorus. Maximum synthesis appeared to occur at an incubation temperature somewhere between 25 and 45°C. Some synthesis occurred at 7°C. In soils adjusted to different pH values, the optimum pH for synthesis appeared to be between pH 5.5 and 7.5. Synthesis of organic phosphorus was increased by repeated wetting and drying or freezing and thawing of soils, although the effect of the latter was of questionable significance.

Synthesis of organic phosphorus in 1 week in 41 noncalcareous soils was associated to only a minor extent with the content of organic carbon, total nitrogen, and organic phosphorus, and not significantly with pH and the content of inorganic phosphorus. Its association with these factors did not increase greatly when the soils were preincubated for 1 week without P³²

prior to incubation for 1 week with P^{32} and measurement of synthesis. Synthesis of organic phosphorus varied from 0.59 to 3.56 ppm of phosphorus in the pre-incubated soil samples and from 0.69 to 6.23 ppm in the samples not pre-incubated.

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BIOLOGICAL TRANSFORMATIONS OF PHOSPHORUS IN SOIL

III. ESTIMATION OF AVAILABLE SOIL PHOSPHORUS *)

by C. A. I. GORING and J. A. ZOELLNER **)

INTRODUCTION

Many chemical and biological procedures have been proposed for estimating the availability of soil phosphorus to plants ⁵⁾⁶⁾. The chemical methods generally involve extraction and determination of a small fraction of the inorganic phosphorus. The biological procedures usually involve measurement of growth or phosphorus uptake by plants or micro-organisms.

Fried and Dean ²⁾ recently outlined a new concept of nutrient availability based on the relative amounts of a nutrient absorbed by plants from the soil and from added fertilizer containing an isotope of the nutrient element as a tracer. The availability of the nutrient in the soil is measured in terms of the availability of the nutrient in the fertilizer. Goring ³⁾ pointed out that an analogous measure may be obtained by determining the relative amounts of the nutrient absorbed by soil organisms, and described certain techniques suitable for accomplishing this purpose.

The present paper reports measurements of availability of soil phosphorus to soil organisms in a number of soils. Relationships between these measurements, soil phosphorus available to higher plants as measured by the method of Fried and Dean ²⁾, and chemical fractions of soil phosphorus are described.

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**) Formerly Soil Scientist, U.S. Department of Agriculture, and Collaborator, Iowa Agricultural Experiment Station, now Soil Scientist, Dow Chemical Company, Seal Beach, California; and Graduate Assistant, Iowa State College.

METHODS

Methods for determining total organic phosphorus ³⁾, total inorganic phosphorus ⁴⁾, soil phosphorus available to soil organisms ³⁾, synthesized organic phosphorus ³⁾, soil phosphorus available to higher plants ²⁾, and pH ⁴⁾ have already been described. Method 1A was used for determining Bray and Kurtz ¹⁾ inorganic phosphorus. All analytical results are expressed on the basis of air-dry soil.

Some of the properties of the 40 noncalcareous soils employed in this study have already been tabulated ⁴⁾. Certain additional properties are listed in Table I. Values for soil phosphorus available to soil organisms were derived from results obtained in a previous investigation ⁴⁾. Values for synthesized organic phosphorus have already been given ⁴⁾. In 18 of the soils, values for soil phosphorus available to higher plants were calculated from data reported by Dean ^{*}). These data were obtained from a greenhouse experiment, in which the test crop was millet and the standard fertilizer was monobasic calcium phosphate containing P³².

RESULTS AND DISCUSSION

Table I shows soil phosphorus available to soil organisms (*Y*) in each of 40 soils incubated with 10 and 75 ppm of inorganic phosphorus containing P³². The multiple regression equation expressing the relationship between phosphorus available to soil organisms and six independent variables is as follows, where the figures directly below the regression coefficients are the standard errors associated with the respective coefficients:

$$Y = -18.0 + 0.0122x_1 + 0.0351x_2 + 0.0152x_3 \\ \pm 0.0122 \quad \pm 0.0275 \quad \pm 0.0187 \\ + 1.88x_4 + 2.79x_5 + 3.79x_6 \quad R = 0.894^{**}) \\ \pm 0.33 \quad \pm 2.79 \quad \pm 1.11$$

In this equation, x_1 = total organic phosphorus; x_2 = total inorganic phosphorus minus inorganic phosphorus extracted in the

^{*}) Dean, L. A. Uniform phosphorus experiments: cooperative studies on the fertility status of soils. Unpublished manuscript. Bureau of Plant Industry, Soils, and Agricultural Engineering, U.S. Department of Agriculture.

^{**}) Significant at the 1 percent level.

TABLE I

Properties of the soil samples employed							
Soil sample no.	Soil phosphorus fractions †)				Soil P available to soil organisms		Soil P available to plants (Y_2)
	x_1	x_2	x_3	x_4	Soils incubated directly with P^{32} (Y)	Soils incubated without P^{32} prior to drying and incubation with P^{32} (Y_1)	
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
F 729	366	48	445.0	21.0	82.2	71.3	
F 734	368	62	166.5	3.5	26.8	21.0	
F 735	457	52	224.0	5.0	38.2	35.7	
F 738	323	44	165.7	3.3	18.8	27.1	
F 740	130	18	145.5	6.5	27.5	28.8	
F 743	490	59	247.0	6.0	27.8	19.7	
F 750	296	64	244.5	7.5	31.4	47.7	
F 767	102	50	52.5	1.5	25.2	24.4	
F 770	70	63	67.7	4.3	19.4	16.5	
F 773	155	68	333.0	20.0	54.5	36.4	
F 1515	109	60	93.5	3.5	14.4	10.5	
F 1516	153	79	122.0	3.0	28.3	30.2	
F 1517	185	40	132.2	3.8	25.9	30.8	
F 1518	228	5	165.5	4.5	28.3	24.5	
F 1520	290	119	147.5	5.5	27.9	27.8	
47867	125	13	457.5	12.5	61.2	43.2	
E 787	180	301	283.5	2.5	51.6	38.4	
45642	24	49	36.5	0.5	4.0	7.9	
51119	527	114	468.5	11.5	63.3	49.6	
51112	272	187	189.5	5.5	49.4	37.2	
47871	112	28	373.7	3.3	11.4	9.0	
46264	125	251	690.5	24.5	55.0	80.8	
F 1528	251	29	198.0	6.0	33.1		42.3
F 1530	338	72	220.5	13.5	29.2		70.0
F 1532	294	57	173.7	3.3	12.9		25.7
F 1534	281	13	300.0	10.0	43.7		76.0
F 1536	403	43	225.0	5.0	27.8		41.5
F 1538	450	62	236.0	4.0	28.8		37.1
F 1540	133	43	312.5	7.5	30.5		39.4
F 1542	191	54	219.5	11.5	30.9		50.8
F 1544	114	102	78.5	1.5	15.5		22.3
F 1546	266	74	368.0	28.0	87.5		184.0
F 1548	323	96	183.2	1.8	26.2		33.2
F 1550	468	73	218.0	9.0	32.0		58.5
F 1556	561	78	179.1	5.9	24.6		39.6
F 1558	133	78	173.5	3.5	20.0		50.8
F 1560	152	74	251.5	18.5	38.0		90.2
F 1562	170	68	154.2	1.8	18.5		27.8
F 1564	310	65	122.0	3.0	18.7		24.0
F 1566	305	59	110.0	1.8	15.7		21.8

†) x_1 = Total organic phosphorus. x_2 = Total inorganic phosphorus minus inorganic phosphorus extracted in the determination of organic phosphorus. x_3 = Inorganic phosphorus extracted in the determination of organic phosphorus minus inorganic phosphorus extracted by the dilute NH_4F-HCl extractant of Bray and Kurtz. x_4 = Inorganic phosphorus extracted by the dilute NH_4F-HCl extractant of Bray and Kurtz. (These analyses were made by the Iowa State College Soil Testing Laboratory).

procedure for extracting organic phosphorus; x_3 = inorganic phosphorus extracted in the procedure for extracting organic phosphorus minus inorganic phosphorus extracted by the method of Bray and Kurtz; x_4 = inorganic phosphorus extracted by the method of Bray and Kurtz; and x_5 = pH. For this regression, synthesized organic phosphorus in soils incubated directly with P^{32} was considered to be a possible independent variable influencing the availability of soil phosphorus to soil organisms and was designated as x_6 . It will be noted that $x_1 + x_2 + x_3 + x_4$ = total soil phosphorus.

It was found that for predicting Y , the variables x_1 , x_2 , x_3 , and x_5 were of no appreciable value. This is evidenced by the fact that the multiple regression of Y on x_4 and x_6 yielded a multiple correlation coefficient only slightly lower than that achieved by the regression of Y on all six independent variables. The equation expressing the relationship between Y and the independent variables x_4 and x_6 was found to be

$$\begin{aligned} \hat{Y} &= 3.44 + 2.17x_4 + 4.67x_6 & R &= 0.876^{**}) \\ &\pm 0.21 \quad \pm 1.03 \end{aligned}$$

Both regression coefficients were significant at the 1 percent level. These results indicate that fractions x_4 and x_6 are the important associates of the phosphorus available to soil organisms.

The significant contribution of Bray and Kurtz phosphorus (x_4) to the regression was expected. The significant contribution of synthesized organic phosphorus (x_6) was of considerable interest because of its connection with organic phosphorus mineralization. It appears probable that the significance of organic phosphorus synthesis in the foregoing equation resulted from a correlation between synthesis and mineralization, rather than any direct effect of synthesis on phosphorus availability. Synthesis and mineralization are necessarily closely correlated if changes in total organic phosphorus are small compared to total synthesis and mineralization⁴⁾; a substantial correlation may exist even when relatively large changes in total organic phosphorus occur.

It was reported previously⁵⁾ that synthesized organic phosphorus was virtually independent of total inorganic phosphorus. The low correlation ($r = -0.01$) between the variables x_4 and x_6 indicates that synthesized organic phosphorus also was virtually independent

of Bray and Kurtz inorganic phosphorus. This behavior is evidence in support of one of the basic assumptions made in calculating availability of soil phosphorus to soil organisms⁴), namely, that the amount of organic phosphorus synthesized is independent of the availability of the inorganic phosphorus in the soil.

Table I shows also the soil phosphorus available to soil organisms in 22 soils incubated 1 week at 25°C without addition of P³², followed by drying and incubation with 12.5 and 94 ppm of inorganic phosphorus containing P³². The multiple regression equations expressing the relationship between soil phosphorus available to soil organisms, Bray and Kurtz inorganic phosphorus, and synthesized organic phosphorus for these 22 soils are as follows: For soils incubated directly with P³²

$$\hat{Y} = 3.42 + 2.11x_4 + 5.69x_6 \quad R = 0.891 \text{ **})$$

$$\pm 0.31 \quad \pm 1.27$$

For soils incubated without P³² prior to drying and incubation with P³²

$$\hat{Y} = 5.88 + 2.10x_4 + 6.08x_6' \quad R = 0.871 \text{ **})$$

$$\pm 0.30 \quad \pm 2.20$$

where x_6' is the synthesized organic phosphorus in soils incubated without P³² prior to drying and incubation with P³². The regression coefficient associated with synthesized organic phosphorus (x_6') was significant at the 5 percent level, and all other regression coefficients were significant at the 1 percent level, in agreement with the behaviour observed for the entire group of 40 soils.

The average amounts of soil phosphorus available to soil organisms were 35.1 ppm in the soil incubated directly with P³² and 32.7 ppm in the soils incubated without P³² prior to drying and incubation with P³². The lower availability in the preincubated samples may have resulted from a decrease in availability of inorganic phosphorus, a decrease in mineralizable organic phosphorus or both. In any event, it appears that mineralization of organic phosphorus during the preincubation period did not result in a net increase in availability of soil phosphorus to soil organisms.

Table I shows soil phosphorus available to plants in 18 of the soils. The correlation coefficient between soil phosphorus available to soil organisms on direct incubation with P³² and soil phosphorus

available to plants was 0.819 **). The equations expressing the dependence of soil phosphorus available to soil organisms (Y) and of soil phosphorus available to plants (Y_2) on inorganic phosphorus extracted by the Bray and Kurtz method (x_4) and synthesized organic phosphorus (x_6) were found to be:

$$\begin{aligned} \hat{Y} &= 11.0 + 1.35x_4 + 2.38x_6 & R &= 0.821 ** \\ &\pm 0.27 \quad \pm 1.08 \\ \hat{Y}_2 &= 20.4 + 3.76x_4 & r &= 0.909 ** \\ &\pm 0.45 \end{aligned}$$

In the former equation, the regression on x_4 was significant at the 1 percent level and the regression on x_6 was significant at the 5 percent level. In the latter equation, the contribution of x_6 in the presence of x_4 was found to be nonsignificant. The remaining equation with x_4 was significant at the 1 percent level.

The results obtained in the analysis of the data on the 18 soils are similar to those obtained previously on all 40 soils in that soil phosphorus available to soil organisms depended significantly on both inorganic phosphorus extracted by the Bray and Kurtz method and synthesized organic phosphorus. The fact that synthesized organic phosphorus was of significant value in predicting availability to soil organisms but not to plants is worthy of further consideration. It was suggested above in connection with the results on all 40 soils that the significance of synthesized organic phosphorus resulted from its probable correlation with mineralized organic phosphorus. The greater importance of organic phosphorus synthesis in predicting the availability of phosphorus to soil organisms than to plants may have been associated with greater utilization of mineralized phosphorus by soil organisms than by plants. Such a difference between soil organisms and higher plants with respect to the importance of organic phosphorus mineralization might be accounted for on the basis that soil organisms are more closely associated with mineralization than are higher plants from the standpoint of both operation and position.

SUMMARY AND CONCLUSIONS

Phosphorus available to soil organisms in 40 noncalcareous soils was estimated by an isotope-dilution method. The dependence of phosphorus availability on pH, organic phosphorus synthesized during incubation,

and four different phosphorus fractions was investigated using techniques of multiple linear regression.

Only organic phosphorus synthesized during incubation and inorganic phosphorus extracted from the soils by the dilute $\text{NH}_4\text{F-HCl}$ extractant of Bray and Kurtz were of significance in predicting soil phosphorus available to soil organisms. It was presumed that the observed relationship between phosphorus availability and organic phosphorus synthesis resulted from a correlation of the latter with organic phosphorus mineralization.

Data on 22 soils showed that preincubation decreased both synthesis of organic phosphorus and phosphorus available to soil organisms.

Data on 18 soils showed that measurements of plant-available phosphorus by the technique of Fried and Dean depended significantly on the inorganic phosphorus extracted by the Bray and Kurtz method; they did not depend significantly on organic phosphorus synthesized during incubation. In the same soils, however, phosphorus available to soil organisms depended significantly on both synthesized organic phosphorus and Bray and Kurtz inorganic phosphorus. The difference between higher plants and soil organisms in this respect may have resulted from the more intimate operational and positional association of the latter with organic phosphorus mineralization.

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THE EFFECT OF VARIED NUTRIENT LEVELS ON THE CONCENTRATION AND DISTRIBUTION OF MANGANESE WITHIN THE POTATO PLANT *)

by E. W. BOLLE-JONES **)

INTRODUCTION

Evidence was recently published to show that iron and potassium are interrelated in the metabolism of the potato plant (Bolle-Jones¹⁾). It was shown that potato plants maintained at low levels of iron became chlorotic in the presence of calcium carbonate or at high phosphorus levels or when potassium was deficient. This chlorosis was cured in each instance by the addition of high levels of potassium. The ameliorative effect of potassium on iron deficiency chlorosis was due to an increased efficiency of iron utilisation in chlorophyll formation and to an increased iron content of the laminae.

Advantage was taken of the plant material afforded by the comprehensive experiments undertaken to investigate the iron-potassium interrelationship to determine the effect of nutrient levels on the concentration and distribution of manganese within the plant. The plants were all supplied with sufficient manganese to meet the requirements of normal growth and manganese deficiency symptoms were not observed during the course of the experiments. Therefore the relationships and trends described below deal exclusively with variations detected by chemical analysis and not by visual observation. The trends observed, however, would probably be applicable to plants maintained at lower levels of manganese at which the addition of high levels of iron, phosphorus or calcium carbonate, as described below, might be expected to induce the appearance of manganese deficiency symptoms.

*) These studies were carried out at Long Ashton Research Station and comprise part of the data submitted in a PH. D. Thesis to the University of Bristol in 1952.

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The results given below were obtained by growing potato plants in sand culture under varying levels of iron, potassium, phosphorus and calcium carbonate supplies. It was found that the levels of most of the variables examined markedly influenced the concentration of manganese in the tissues and the distribution of manganese within the plant.

EXPERIMENTAL

Potato plants (variety Majestic, certified Scotch seed tubers) were grown in three factorial experiments conducted in three successive years; the culture technique employed will be described elsewhere (Bolle-Jones²).

In the 1948 experiment four levels of iron were given at each of four levels of potassium with or without calcium carbonate. The iron and potassium levels were chosen to represent severe deficiency (Fe_1 and K_1), mild deficiency (Fe_2 and K_2), normal (Fe_3 and K_3) and luxury (Fe_4 and K_4) consumption. These concentrations are given as milligram-equivalents per litre in Table I. Each treatment received a supply of soluble calcium. In addition, one half of the pots, C_2 treatments, each received 50 g of "Analar" grade calcium carbonate which was well mixed with the sand ($9\frac{1}{2}$ kilograms per pot) prior to planting; treatments not receiving calcium carbonate were designated C_1 . The tubers were planted on the tenth of May 1948.

The 1949 experiment was designed to include three levels each of iron, potassium and phosphate which were chosen to represent deficiency (Fe_1 , K_1 and P_1), normal (Fe_2 , K_2 and P_2) and luxury

TABLE I

Nutrient levels of iron (Fe), potassium (K), and phosphate (P), expressed as milligram-equivalents per litre

	1948	1949	1950		1948	1949	1950		1948	1949	1950
Fe_1	0.0005	0.0024	approx. 0.0016	K_1	0.50	0.60	0.60	P_1	—	0.90	0.90
Fe	0.0075	0.0600	—	K_2	1.25	2.40	—	P_2	4.00	2.70	—
Fe_2	0.1125	1.50	1.00	K_3	3.12	9.60	9.60	P_3	—	8.10	8.10
Fe_4	1.6875	—	—	K_4	7.81	—	—		—	—	—

(Fe_3 , K_3 and P_3) consumption. The concentrations of these nutrients which were applied are given in Table I. The tubers were planted on the twenty-fifth of May 1949.

In the 1950 experiment iron, potassium and phosphate were each

applied at two levels chosen to represent deficiency (Fe_1 , K_1 and P_1) and luxury (Fe_3 , K_3 and P_3) consumption. The potassium and phosphate levels were identical with those of the 1949 experiment, Table I. The tubers were planted on the second of May 1950.

Throughout these experiments manganese (Mn^{++}) was applied at a concentration of 0.02 milligram-equivalents per litre.

In the 1948 and 1949 experiments laminae required for chemical analysis, were taken from young and old regions of the plant. The "young" laminae were sampled at the third and fourth nodes from the shoot tip while the "old" laminae were those taken from the midstem region; these were not senescent laminae but were those which showed early potassium deficiency symptoms. Monthly samplings were taken throughout the growing season. The new tubers were analysed for both experiments as well as the roots for the 1949 experiment.

In the 1950 experiment all plants grown in Blocks 7 and 8 (each block contained a treatment replicate) were completely harvested on the eleventh of June; another two blocks (3 and 4) were similarly harvested on the thirteenth of July. Plants grown in Blocks 3, 4, 7 and 8 were not sampled during the growing period; any fallen leaves were carefully collected and added to the "bottom" region of the shoot at the time of harvest. The aerial shoots of each plant were, on harvesting, subdivided into three regions, according to length:

- (a) the *Top* region which constitute 1/5,
- (b) the *Middle* region — 2/5,
- (c) the *Bottom* region — which contributed the remaining 2/5.

Each region was further separated into laminae and stems plus petioles prior to being oven-dried. The "young" laminae of the 1948 and 1949 monthly samplings, were taken from areas corresponding to the top region whereas the old laminae were taken partly from the middle and partly from the bottom regions.

The oven-dried tissues were digested with nitric and perchloric acids (B o l l e - J o n e s ²). The manganese content of the digest was, for the 1948 material, determined according to the periodate method of R i c h a r d s ⁶), as modified by N i c h o l a s ⁴), to include phosphoric acid during the oxidation. For the 1949 and 1950 material this method was replaced by the more sensitive procedure of C o r n f i e l d and P o l l a r d ³), who used tetramethyldiamino-diphenyl-methane and periodate reagents; smaller aliquots

of the digest, and no heat treatment, were required for this new method.

RESULTS

The data are not given *in extenso* but only the main trends are summarized; representative results are presented as mean tables which show clearly the overall and interaction effects. A description of the main visual effects and the interactions governing these effects have been given elsewhere (Bolle-Jones¹). In general it was found that when iron supplies were limiting (*i.e.* at the Fe₁ level) iron deficiency chlorosis was induced or accentuated by the addition of calcium carbonate, by the addition of phosphorus, or by a reduction in the supply of potassium. This chlorosis was cured by the addition of high levels of potassium.

A. 1948 experiment

1. *Laminae* (Tables II, III). The addition of iron decreased the manganese content of the old laminae; this effect of iron was much more marked at the C₁ level. At the June sampling, Table II,

TABLE II

Concentration of manganese in old laminae. 1948 Experiment, June sampling.
Mean values expressed as ppm Mn in dry matter

Treatment level	Fe ₁	Fe ₂	Fe ₃	Fe ₄	C ₁	C ₂	Mean
K ₁	28	35	24	21	33	21	27
K ₂	30	32	30	20	36	20	28
		(± 5.06)			(± 3.57)		(± 2.53)
K ₃	30	29	23	19	35	16	25
K ₄	30	26	22	22	34	16	25
C ₁	43	42	29	24	—	—	34
		(± 3.57)					(± 1.79)
C ₂	17	19	21	17	—	—	18
Mean	30	30	25	20	—	—	26
		(± 2.53)					

potassium addition had no marked effect but at the August sampling, Table III, it increased the manganese content of both young and old laminae in the C₁ treatments.

The addition of calcium carbonate decreased markedly the manganese content of both young and old laminae. This effect was much more marked at the lower iron levels in the old laminae.

TABLE III

Concentration of manganese in young and old laminae. 1948 Experiment, August sampling. Mean values expressed as ppm Mn in dry matter

Treatment level	Fe ₁	Fe ₂	Fe ₃	Fe ₄	C ₁	C ₂	Mean
Young laminae							
K ₁	47	35	37	32	49	26	38
K ₂	41	34	55	40	60	25	43
		(± 6.75)			(± 4.77)		(± 3.37)
K ₃	51	40	73	61	83	29	56
K ₄	38	43	31	31	46	26	36
C ₁	57	47	74	60	—	—	60
		(± 4.77)					(± 2.39)
C ₂	32	29	23	22	—	—	26
Mean	44	38	49	41	—	—	43
		(± 3.37)					
Old laminae							
K ₁	52	50	28	24	39	38	38
K ₂	57	47	40	30	46	41	44
		(± 6.89)			(± 4.87)		(± 3.45)
K ₃	72	47	33	34	54	38	46
K ₄	86	56	42	41	69	43	56
C ₁	90	55	33	30	—	—	52
		(± 4.87)					(± 2.44)
C ₂	43	45	38	34	—	—	40
Mean	67	50	36	32	—	—	46
		(± 3.45)					

2. *Tubers*. The application of potassium increased slightly the manganese content at the Fe₁ and C₁ levels but calcium carbonate decreased it particularly at the lower iron levels. These results are not presented here.

Thus in 1948 experiment the effect of increased iron supply was to decrease the manganese content of the laminae; calcium carbonate had a similar effect both on laminae and tuber contents.

B. 1949 experiment

1. *Laminae* (Tables IV, V). The addition of iron decreased the manganese content of young and old laminae.

Increased potassium supply tended to decrease the manganese content of the young laminae of the earlier samplings, Table IV, but later gave well marked increases for both young and old laminae, Table V.

TABLE IV

Concentration of manganese in young and old laminae. 1949 Experiment, July sampling. Mean values expressed as ppm Mn in dry matter

Treatment level	Fe ₁	Fe ₂	Fe ₃	P ₁	P ₂	P ₃	Mean
Young laminae							
	(± 7.55)			(± 7.55)			(± 4.36)
K ₁	107	77	43	86	84	56	76
K ₂	106	75	43	86	72	66	75
K ₃	76	78	37	60	70	59	63
P ₁	97	76	60	—	—	—	77
P ₂	110	79	37	—	—	—	75
P ₃	80	74	27	—	—	—	60
Mean	96	76	41	—	—	—	71
	(± 4.36)						
Old laminae							
	(± 10.23)			(± 10.23)			(± 5.91)
K ₁	156	115	56	129	108	90	109
K ₂	168	130	63	122	127	112	120
K ₃	148	132	61	93	127	121	114
P ₁	153	111	81	—	—	—	115
P ₂	169	130	63	—	—	—	121
P ₃	150	135	37	—	—	—	107
Mean	157	125	60	—	—	—	114
	(± 5.91)						

TABLE V

Concentration of manganese in young and old laminae. 1949 Experiment, September sampling. Mean values expressed as ppm Mn in dry matter

Treatment level	Fe ₁	Fe ₂	Fe ₃	P ₁	P ₂	P ₃	Mean
Young laminae							
	(± 11.3)			(± 11.3)			(± 6.5)
K ₁	114	75	52	108	77	56	80
K ₂	126	85	69	128	70	82	93
K ₃	108	123	76	130	87	90	102
P ₁	155	114	97	—	—	—	122
P ₂	96	93	45	—	—	—	78
P ₃	97	76	55	—	—	—	76
Mean	116	94	65	—	—	—	92
	(± 6.5)						
Old laminae							
	(± 14.0)			(± 14.0)			(± 8.1)
K ₁	173	96	69	142	110	88	113
K ₂	219	125	96	182	148	110	147
K ₃	171	164	87	155	140	109	141
P ₁	213	155	112	—	—	—	160
P ₂	183	134	75	—	—	—	132
P ₃	163	97	65	—	—	—	108
Mean	188	129	84	—	—	—	134
	(± 8.1)						

Increased phosphorus supply decreased the manganese content of both young and old laminae.

The manganese content of the young was less than that of the old laminae; this disparity was usually greatest in the P_0 treatment.

2. **Tubers** (Table VI). The manganese content of the tubers was reduced by increased supplies of phosphorus; this effect, which was the only well marked trend, was significant at the 10% level.

TABLE VI

Concentration of manganese in tubers, 1949 Experiment. Mean values expressed as ppm Mn in dry matter

Treatment	K ₂	Fe ₂	Fe ₃	P ₁	P ₂	P ₃	Mean
		(= 0.787)		(= 0.787)			(= 0.455)
P_0	—	3.0	2.7	3.1	3.6	2.4	3.0
P_1	—	3.1	5.0	4.7	2.6	2.6	3.3
K_2	3.1	5.1	5.2	6.6	4.2	2.6	4.4
P_2	2.9	5.4	6.1	—	—	—	4.8
P_3	3.5	2.7	4.3	—	—	—	3.5
P_4	1.9	3.1	2.5	—	—	—	2.5
Mean	2.8	3.7	4.3	—	—	—	3.6
		(= 0.455)					

3. **Roots** (Table VII). The manganese content of the roots, unlike that of the laminae, showed an overall increase on the addition of iron. Phosphorus addition decreased the manganese content of the roots.

TABLE VII

Concentration of manganese in roots, 1949 Experiment. Mean values expressed as ppm Mn in dry matter

Treatment	K ₂	Fe ₂	Fe ₃	P ₁	P ₂	P ₃	Mean
		(= 15.4)		(= 15.4)			(= 15.4)
P_0	—	225	225	225	225	225	225
P_1	—	225	225	225	225	225	225
P_2	—	225	225	225	225	225	225
P_3	—	225	225	225	225	225	225
P_4	—	225	225	225	225	225	225
K_2	14	257	257	—	—	—	257
P_5	—	178	225	—	—	—	225
Mean	—	230	225	—	—	—	225
		(= 15.4)					

Potassium addition evoked no significant effect.

Thus in the 1949 experiment increased iron supply decreased the manganese content of the laminae but increased that of the roots.

TABLE VIII
Concentration of manganese in the laminae, stems and petioles, new tubers, mother tubers and roots. 1950 Experiment.
Blocks 3 and 4 (except for the mother tubers). Mean values expressed as ppm Mn in dry matter

Portion analysed	Standard error	Treatment levels														Mean		
		Fe ₁		Fe ₃		K ₁		K ₃		P ₁		P ₃		P ₁	P ₃		Mean	
		K ₁	K ₃	K ₁	K ₃	P ₁	P ₃	P ₁	P ₃	Fe ₁	Fe ₃	Fe ₁	Fe ₃					
Laminae (top, middle and bottom)	± 4.80 ± 3.39	78 73	68 73	41 45	48 45	69 60	50 60	60 58	55 53	75 65	55 53	71 53	35 59					
Stems and petioles (top, middle and bottom)	± 5.92 ± 4.18	69 76	83 76	43 60	77 60	70 56	42 91	69 80	83 80	77 43	68 56	43 68						
New tubers	± 0.83 ± 0.59	16.4 12.6	8.9 12.6	8.4 9.3	10.1 9.3	9.7 12.4	15.1 9.9	9.9 9.5	9.1 9.8	9.8 9.8	15.4 12.1	8.8 11.0						
Mother tubers (Blocks 3, 4, 7 and 8)	± 2.12 ± 1.50	37 30	24 30	29 26	23 26	30 33	36 24	23 24	27 26	26 30	34 26	28						
Roots	± 6.96 ± 4.92	102 132	163 132	276 266	257 266	236 189	141 210	259 210	161 168	327 248	96 151	206 199						

increased phosphorus supply decreased the manganese content of laminae, tubers and roots; increased potassium supply increased, towards the end of the experiment, the manganese content of the laminae but exerted no significant effect on either tubers or roots.

C. 1950 experiment

1. Nutrient concentrations in different regions of the plant. The results reported here are for the July sampling (Blocks 3 and 4) only as they would be more likely to illustrate the effect of treatment on manganese concentration in various regions, than would the earlier sampling (Blocks 7 and 8). The data reported in this section, as in the previous sections, represent concentrations in the plant and are expressed as parts per million of manganese in dry matter (Table VIII).

Laminae. The addition of iron or phosphorus reduced the manganese content. These treatment effects, which were significant did not vary with region. The laminae of the lower regions however contained significantly more manganese than those of the top but these data are not presented separately here.

Stems and petioles. The manganese content of the stems and petioles, unlike the laminae, did not vary significantly with region; the effect of treatment was also independent of region. Increased potassium supply increased while iron and phosphorus decreased the manganese content; the K, P and Fe effects were significant at the 1.0% and 5.0% levels respectively.

New tubers. The overall effect of treatments on manganese content was significant at the 0.1% level. The Fe, K and P main effects were significant but of greater interest were the highly significant FeK, FeP, and KP interaction effects. The depressive effect of iron level on manganese content was always more marked in the K_1 and P_3 treatments and the beneficial effect of phosphorus level in the K_1 treatments.

Mother tubers. Increased potassium supply decreased the concentration of manganese in the mother tubers; this effect, significant at the 1.0% level, suggested that potassium enhanced the withdrawal of manganese from the tubers by the growing plants. Other effects were not significant. The results given in Table VIII are means of

TABLE IX
Manganese content of laminae, stems and petioles, roots and complete plants. 1950
Experiment. Blocks 7 and 8. Mean values expressed as micrograms Mn per unit of four plants

Portion analysed	Standard error	Treatment levels												Mean						
		Fe ₁			Fe ₃			K ₁			K ₃				P ₁			P ₃		
		K ₁	K ₃	Fe ₁	K ₁	K ₃	Fe ₃	P ₁	P ₃	K ₁	K ₃	Fe ₁	P ₁		P ₃	Fe ₁	Fe ₃	P ₁	Fe ₁	Fe ₃
Laminae (top, middle and bottom)	± 29.1	752	669	376	379	618	511	511	537	766	364	656	391	544						
	± 16.8	711		378		564		524		565		524								
Stems and petioles (top, middle and bottom)	± 26.3	433	664	260	429	439	254	591	502	645	384	452	304	446						
	± 18.6	548		344		346		546		514		378								
Roots	± 154	1772	2079	2276	1653	2102	1946	2082	1650	2071	2113	1780	1816	1945						
	± 109	1926		1964		2024		1866		2092		1798								
Complete plants	± 247	5352	6116	4211	4136	5304	4259	5439	4813	6349	4395	5120	3952	4954						
	± 175	5734		4174		4782		5126		5372		4536								

values obtained for Blocks 3, 4, 7 and 8; the interaction, "months $\times$ treatments", (between the June and the July samplings) was not significant.

Roots. The addition of iron caused an overall increase in the manganese content whereas phosphorus decreased it; both effects were consistent and highly significant. The addition of potassium increased the manganese content at the Fe_1 level but decreased it at the Fe_3 level; the FeK interaction effect was significant at the 0.1% level.

The effects of nutrient level on the concentration of manganese in the tissues noted in the 1950 experiment generally confirmed those of the two preceding years. Thus: increased iron supply reduced the manganese content of the laminae, stems and petioles and new tubers but increased that of the roots; increased phosphorus supply decreased the manganese content of the laminae, stems and petioles and the roots; increased potassium supply increased the manganese content of the stems and petioles but decreased that of the mother tuber.

2. *Total nutrient content of different regions of the potato plant.* The results reported below (Table IX) have been derived from the concentration of manganese in the tissues and from the yield data. They are therefore expressed as micrograms (μg) per region. The data obtained from Blocks 7 and 8 (June sampling) were chosen for the following description, as the effect of treatment on yield, although apparent, was not as marked as in Blocks 3 and 4 (July sampling). Consequently any differences in the nutrient content of any region of the potato plant were more likely to be attributed to the direct effect of treatment on uptake and accumulation of nutrients than to growth effects.

Laminae. Increased supplies of iron markedly decreased the manganese content of the laminae of all regions. The addition of phosphorus decreased the manganese content at the Fe_1 and K_1 levels but had no significant effect at the Fe_3 and K_3 levels; both the FeP and the KP interaction effects were significant. The effect of iron level varied significantly with region; the full data are not presented here but they showed that the influence of iron was more marked in the bottom than in the top region.

Stems and petioles. The manganese content increased with in-

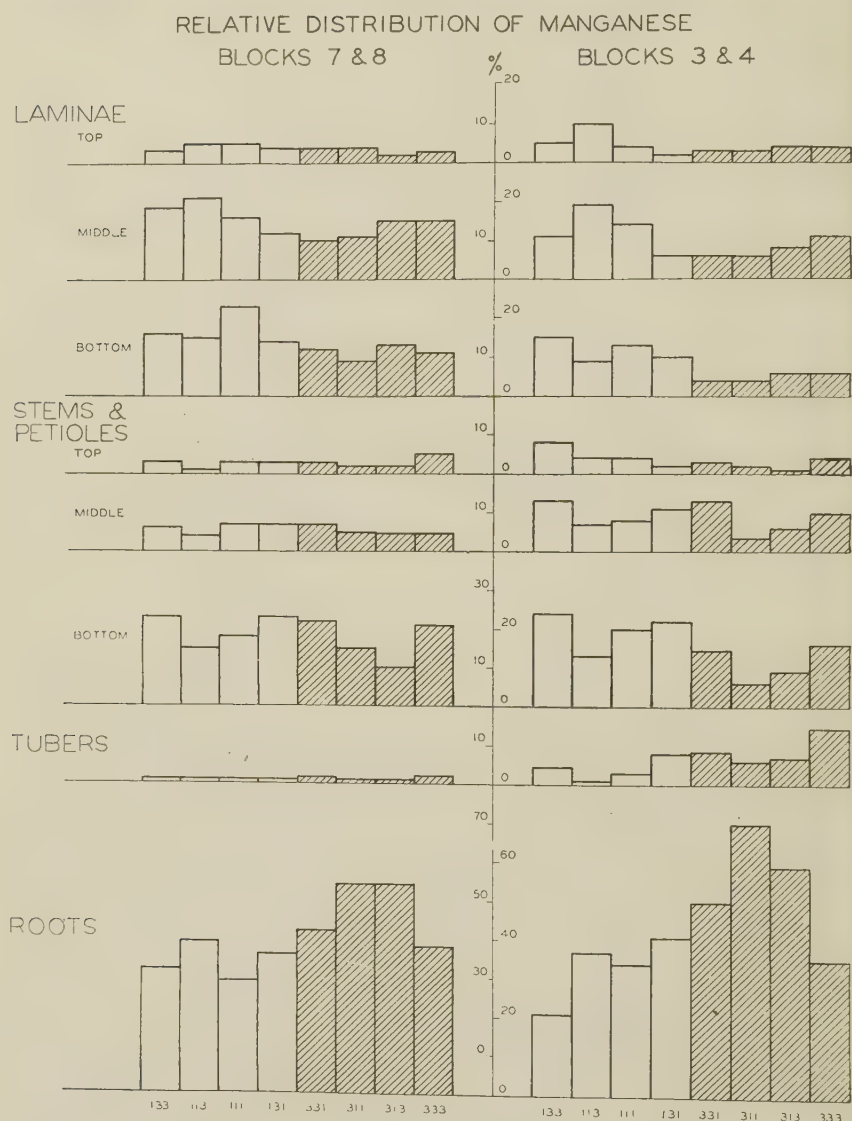


Fig. 1. Relative distribution of manganese within the potato plant 6 weeks (Blocks 7 and 8) and 10 weeks (Blocks 3 and 4) after planting. The respective levels of Fe, K and P applied are indicated beneath the lowest histogram; *e.g.* 133 refers to treatment $Fe_1K_3P_3$.

creased potassium level but decreased with either iron or phosphorus. The effect of extra potassium supply was, unlike that obtained for the laminae, clearly defined and consistently positive. The effects of iron and potassium addition were usually more marked in the lower regions.

New tubers. The manganese content of the tubers, expressed as micrograms per plot, did not vary significantly with treatment and the results are not presented here.

Roots. The addition of iron increased the manganese content of the roots at the K_1 level but decreased it at the K_3 . This FeK interaction effect was significant at the 5.0% level; other treatment effects were not significant.

Complete plants. The addition of either iron or phosphorus decreased the manganese content of the complete plant; increased potassium level exercised no significant effect.

Thus, qualitatively, the effects of nutrient level on the "absolute" manganese content of various regions of the shoot were similar to those governing the concentration of manganese within the tissues. In general, the application of iron or phosphorus decreased the "absolute" manganese content of the aerial shoot whereas potassium addition increased that of the stems and petioles.

3. The relative distribution of manganese within the potato plant. A diagrammatic illustration of the relative distribution is given in Fig. 1. Iron level clearly controlled the distribution of manganese within the plant. Increased iron supply increased the proportion of manganese retained in the roots and in the tubers but decreased the proportion translocated to the aerial shoot system. Increased potassium supply increased the proportion of manganese found in the stems and petioles and the tubers but, with one exception, decreased that found in the roots. Potassium addition therefore appeared to increase the mobility of iron within the plant. The overall effect of potassium level on the distribution of manganese to the laminae was not consistent.

Increased phosphorus supply generally decreased the proportion of manganese found in the roots but increased that of the laminae.

DISCUSSION AND CONCLUSIONS

The addition of either extra iron or phosphorus reduced the intake and hence absorption, of manganese by the plant but potassium had little effect. All three elements exercised important influences on the distribution of manganese within the plant.

Increased iron level generally decreased the proportion of manganese translocated to the shoots and increased that retained in the roots whereas both potassium and phosphorus additions decreased the proportion of iron retained in the roots.

An adequate potassium supply seemed necessary for the efficient mobilisation of manganese within the plant. Thus increased potassium level decreased the concentration of manganese which remained in the mother tubers and increased the proportion of manganese translocated to the newly formed tubers and to the stems and petioles.

✓ Sideris and Young⁷⁾ concluded from their investigation of the interrelationship of iron and manganese in the pineapple that "manganese did not accumulate in the roots but was translocated to the leaves". This observation was however presumably based on the *concentration* of manganese found in the root tissues and not on the "absolute" amount of manganese or its proportion (of that present in the whole plant) found in the roots. Their statement did not take into consideration the effect of the varying levels of iron and manganese on growth and tissue production, and hence, the total amount of manganese present in the roots relative to the complete plant. It was clear however, from the present experiments, that increased iron level not only increased the concentration but also the proportion of manganese found in the roots of the potato.

There was no evidence, in the present work, to suggest that high iron levels precipitated manganese on the outside of the roots and thus give disproportionately high values for manganese concentration. In fact, Olsen⁵⁾ showed that unlike iron, manganese is not made unavailable by precipitation in alkaline nutrient media. If such precipitation was an important factor the application of phosphorus would have been expected to increase the manganese concentration found for the roots but the reverse was true. It was more likely that the high concentration of iron known to occur within the roots at these high iron levels (Bolle-Jones, un-

published) was directly responsible for the immobilisation or retention of manganese in order to maintain a favourable Fe/Mn balance (Somers, Gilbert and Shive⁸); Twyman⁹)).

The addition of calcium carbonate markedly reduced the manganese content of the laminae (as was found by Nicholas⁴)) and tubers, particularly at the lower iron levels. It also probably affected the distribution of manganese within the plant but no data are available to corroborate this suggestion.

Whereas the concentration of manganese found in the laminae varied with region and was usually highest in the old or the bottom region laminae no such significant variation was found for the stems and petioles. This might indicate, for the stems and petioles, a freedom of movement of manganese which seemed to be lacking in the laminae which appeared to accumulate manganese.

The effect of potassium level on the concentration of manganese in the laminae usually changed with time. At the earlier samplings potassium addition decreased the concentration of manganese in the laminae but later this effect was reversed. This fact might imply that in the earlier samplings sufficient manganese was available to meet immediate growth requirements but later in the season due to the accumulation and, presumably, retention of manganese in the old laminae an increased potassium level was necessary to maintain and enhance the mobility of newly absorbed manganese within the plant and to increase its availability to the growing regions.

SUMMARY

1. Potato plants were grown in sand culture with varying levels of iron, potassium, phosphorus and calcium carbonate and an adequate supply of manganese. The concentration and distribution of manganese in various parts of the plant were examined at intervals throughout the growing season.

2. Increased iron supply decreased the concentration of manganese of the laminae and stems and petioles but increased that of the roots; iron application also decreased the uptake of manganese by the plant.

3. Increased potassium supply increased the concentration of manganese in the stems and petioles and also in the laminae late in the season after having caused a decrease at the beginning of the growth period. Potassium level had no marked effect on manganese uptake.

4. Increased phosphorus supply decreased the uptake of manganese by the plant and decreased its concentration in the laminae, stems and petioles and roots.

5. The addition of calcium carbonate decreased the concentration of manganese found in the laminae and tubers, especially at iron deficiency levels.

6. Extra potassium or phosphorus generally reduced the proportion of manganese retained in the roots whereas iron addition impeded the translocation of manganese to the shoots and caused an accumulation in the roots.

7. Increased potassium supply increased the proportion of manganese in the newly formed tubers and in the stems and petioles whereas phosphorus increased that of the laminae.

8. It is suggested that one of the functions of potassium was to increase the mobility of manganese within the plant.

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MANGAN, KUPFER UND KOBALT IN PFLANZEN UND BÖDEN SCHLESWIG-HOLSTEINISCHER WEIDEGEBIETE

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In Schleswig-Holstein liegen Anhaltspunkte dafür vor, dass gebietsweise mit Mangan-, Kupfer- und Kobaltmangel im Futter der Weidetiere zu rechnen ist. Manganmangel tritt häufig in Haferbeständen derjenigen sandigen Geestböden auf, deren Reaktion durch zu starke Kalkung in den Bereich über pH 6 angestiegen ist. Da die als Dörrflecken bezeichneten Mangelsymptome des Hafers nach Untersuchungen von Nicholas²¹⁾ das Ergebnis eines zu geringen Mangangehaltes in den oberirdischen Pflanzenteilen sind, war zu erwarten, dass auch das Weidefutter auf derartigen Standorten manganarm ist oder sogar an Manganmangel leidet.

Kupfermangelsymptome sind in den Pflanzenbeständen der Geest nicht so oft wie Manganmangelsymptome zu beobachten. Da die auf der Geest verbreitete Lecksucht der Rinder trotzdem auch auf Kupfermangel zurückgeführt wird²²⁾, musste mit verhältnismässig geringen Kupfergehalten des Weidefutters dieser Landschaftszone gerechnet werden.

Neuerdings ist erwiesen, dass ausserdem Mangelkrankheiten beim Vieh hervorgerufen werden, wenn das Weidefutter zu wenig Kobalt enthält. In Europa liegen derartige Erfahrungen in Norwegen (Ender⁷⁾), Schweden (Svanberg³⁰⁾), Dänemark (Bendixen⁴⁾) und den Niederlanden (t'Hart¹⁰⁾) vor. Auch aus der Lüneburger Heide (Meyer-Bahlburg¹⁹⁾), dem Schwarzwald (Riehm²³⁾) und Schleswig-Holstein werden einzelne Erfolge mit Kobaltfütterung mitgeteilt.

Um eine Vorstellung von den Schwermetallgehalten des Weidefutters und damit Unterlagen für die Beseitigung wichtiger Mangel-

erscheinungen beim Rindvieh zu erhalten, bestimmten wir Mangan, Kupfer und Kobalt im Futter auf verschiedenen Böden.

Ausser den Pflanzenanalysen wurden Bodenuntersuchungen der gleichen Standorte durchgeführt. Hierbei beschränkten wir uns auf die Ermittlung der Gesamtgehalte des Bodens an Mangan, Kupfer und Kobalt und benutzten nicht die teilweise üblichen Verfahren zur Bestimmung löslicher Anteile. Eine Beziehung zwischen löslichen Anteilen und Pflanzengehalten ist nämlich für schleswig-holsteinische Verhältnisse bisher nicht erwiesen. Ausser den erwähnten Gesamtgehalten wurden die pH-Werte und Humusgehalte der Böden gemessen, weil nach Literaturangaben zu vermuten war, dass sie einen Einfluss auf die Pflanzenverfügbarkeit der Schwermetalle Mangan, Kupfer und Kobalt ausüben.

In den folgenden Abschnitten werden zunächst die angewandten Methoden und anschliessend die Ergebnisse der Schwermetallanalysen besprochen.

I. VERSUCHSANSTELLUNG UND CHEMISCHE ANALYSENVERFAHREN

Die Untersuchungen wurden an 56 Dauerweiden ausgeführt. Sie lagen auf Böden, die in Schleswig-Holstein grossflächig verbreitet sind.

TABELLE I

Bodentyp	Zahl der Versuchsweiden
Braunerden	14
Marschböden	5
Podsole	30
Niedermoore	7
Insgesamt	56

Die Braunerden *) haben sich auf Geschiebemergel der jungdiluvialen Moränen des Weichselglazials im Ostteil des Landes gebildet. Auf dem als Geest bezeichneten Mittelrücken entwickelten sich aus Tal- und Vorschüttungssanden des Weichselglazials vor allem schwache bis starke Podsole mit wechselndem Humusgehalt. Die Marschböden entstanden im westlichen Küstenraum aus alluvialen Meeressedimenten. Die untersuchten Niedermoore liegen teils in der Zone der Braunerden (Schlichting²⁶⁾), teils zwischen Podsolon des Mittelrückens.

*) Hinsichtlich der Nomenklatur siehe Kubiśna¹⁴⁾.

TABELLE II

Probe- fläche	Pflanzenart	Fe ppm	Mn ppm	Cu ppm	Co ppm
A	<i>Trif. prat.</i>	79,6	20,2	2,74	0,023
B	<i>Trif. prat.</i>	67,6	18,2	3,69	0,024
A	<i>Lolium per.</i>	77,3	20,5	1,62	0,019
B	<i>Lolium per.</i>	72,2	27,5	2,69	0,020

Um die Futterproben im gleichen Entwicklungszustand ernten zu können und sie ausserdem vor Verunreinigungen durch den Tritt der Weidetiere zu schützen, wurde auf jeder Weide eine 9 m² grosse Parzelle eingezäunt. Von diesen Parzellen wurden Pflanzen- und Bodenproben gezogen. Nur für diese Probeflächen und nicht für die ganzen Weiden gelten die gemessenen Werte. Aus den Tabellen II und III ist nämlich ersichtlich, dass sowohl auf einem Acker (*Lolium perenne*, *Trifolium pratense*) als auch auf einer Weide (Mischprobe) die Schwermetallgehalte der Pflanzen, die an verschiedenen Stellen der Schläge geerntet wurden, erheblich voneinander abweichen können, obgleich die Böden der einzelnen Probeflächen ausgeglichen erschienen.

TABELLE III

Schwermetallgehalte des Weidefutters auf einer Braunerde, humoser sandiger Lehm, pH(KCl) 5,9				
	Eisen ppm	Mangan ppm	Kupfer ppm	Kobalt ppm
Mittelwerte M v. 16 Parzellen	76,2	34,9	5,8	0,037
Mitt. Fehler m.	2,2	2,2	0,2	0,003
Streuung s	8,7	8,7	0,7	0,012

Im Gegensatz hierzu wichen die Schwermetallgehalte von Pflanzen, die innerhalb einer Parzelle zum gleichen Zeitpunkt geerntet wurden, verhältnismässig wenig von einander ab.

Vergleicht man die Schwermetallgehalte vom Weidefutter verschiedener Böden miteinander, so muss man damit rechnen, dass die beobachteten Schwankungen nicht alleine durch unterschiedliche Boden- und Witterungsverhältnisse hervorgerufen werden, sondern dass ausserdem die unterschiedliche botanische Zusammensetzung die Schwermetallgehalte der Mischproben beeinflusst. Nach Untersuchungen von Güttler⁹⁾, Gisiger⁸⁾, Hasler¹¹⁾ und Arthur¹⁾ enthalten nämlich verschiedene Pflan-

zenarten und — Sorten auf dem gleichen Standort teilweise sehr unterschiedliche Mineralstoffmengen.

Um festzustellen, ob und in welchem Ausmass diese Feststellungen auf die untersuchten Weiden übertragen werden können, wurden auf je einem Niedermoor- und Podsolstandort die vorherrschenden Pflanzenarten zum gleichen Zeitpunkt, also nicht gleichem Entwicklungszustand, geerntet und untersucht. Aus Tabelle IV ist ersichtlich, dass auch auf den Weiden verschiedene Pflanzen unterschiedliche Schwermetallmengen enthalten.

TABELLE IV

Versuchsweide	Pflanzenart	Fe ppm	Mn ppm	Cu ppm	Co ppm
stark erdiges, gut bis mässig zersetz- tes Niedermoor. Probefläche: 40 qm Erntedatum: 27.5.1952	<i>Holcus lanatus</i>	61,0	164,0	6,83	0,021
	<i>Alopec. prat.</i>	52,6	77,3	5,35	0,019
	<i>Phleum prat.</i>	46,3	55,8	5,96	0,018
	<i>Bromus mollis</i>	48,1	49,2	5,41	0,018
	<i>Arrhen. elat.</i>	48,6	78,5	3,92	0,025
	<i>Lotus corn.</i>	66,8	50,1	5,98	0,015
Humus-Gley- Podsol. Probefläche: 36 qm Erntedatum: 29.5.52	<i>Vicia sep.</i>	105,9	54,1	5,43	0,037
	<i>Holcus lanatus</i>	45,6	333,7	6,24	0,015
	<i>Alopec. prat.</i>	56,4	103,7	4,26	0,027
	<i>Arrhen. elat.</i>	43,4	85,7	3,21	0,015
	<i>Anthox. odor.</i>	59,6	358,7	4,52	0,026
	<i>Poa trivialis</i>	53,2	110,2	6,59	0,021
	<i>Festuca elat.</i>	42,5	116,0	5,22	0,017
	<i>Trifolium prat.</i>	62,3	90,0	6,94	0,028

TABELLE V

Bodentyp	Pflanzenart	Fe ppm	Mn ppm	Cu ppm	Co ppm
Podsol	<i>Lolium per.</i>	62,5	16,2	2,50	0,019
	<i>Trif. prat.</i>	74,7	33,4	3,57	0,026
Podsol	<i>Lolium per.</i>	60,3	48,0	1,62	0,019
	<i>Trif. prat.</i>	78,6	20,2	2,74	0,023
mesotr. Braunerde	<i>Lolium per.</i>	42,3	86,3	4,00	0,044
	<i>Trif. prat.</i>	66,8	63,1	5,25	0,073
eutroph. Braunerde	<i>Lolium per.</i>	54,8	45,0	5,25	0,027
	<i>Trif. prat.</i>	91,5	60,0	6,87	0,032
eutroph. Braunerde	<i>Lolium per.</i>	23,9	23,5	4,75	0,025
	<i>Trif. prat.</i>	39,8	30,1	5,50	0,032

Nach den in der Literatur mitgeteilten Analysenergebnissen musste man annehmen, dass Leguminosen durchschnittlich mehr Schwermetalle als Gramineen enthalten. Auf der Weide scheint dies nach Tabelle IV nicht allgemein zuzutreffen. Wohl aber

besitzt auf verschiedenen Äckern, wie aus Tabelle V ersichtlich ist, *Lolium perenne* stets weniger Eisen, Kupfer und Kobalt als *Trifolium pratense*. Mangan macht teilweise eine Ausnahme.

TABELLE VI

Probe	Fe ppm	Mn ppm	Cu ppm	Co ppm
<i>Holcus lanatus</i>	73,6	295,0	5,98	0,072
Mischprobe	77,1	185,0	6,03	0,021

Verglichen mit den übrigen Pflanzen ist *Holcus lanatus* auf beiden Standorten der Tabelle IV besonders manganreich. Diese Eigenart wurde auch auf einem weiteren Podsolstandort (Tabelle VI) festgestellt.

Aus den Ergebnissen der Tabellen IV–VI ist zu entnehmen, dass der Schwermetallgehalt der Weidefuttermischprobe durch die botanische Zusammensetzung beeinflusst wird. Aus Tabelle V ist aber gleichzeitig abzulesen, dass beide Pflanzen auf den Podsolen weniger Kupfer und Kobalt als auf den Braunerden enthalten. Ähnliche Ergebnisse erzielten wir beim Weidefutter. Die bei ihm gemessenen Unterschiede müssen daher mehr den Einflüssen des Bodens als der unterschiedlichen botanischen Zusammensetzung des Futters zugeordnet werden.

Um repräsentative Mischproben zu erhalten, wurde das Futter an fünf oder sechs Stellen der Versuchsparzellen mit einer Viehschere geerntet und zu einer Probe vereinigt. Eine Schwermetallverunreinigung durch die Schere war nicht nachzuweisen. Mit der Viehschere konnte das Futter stets in gleicher Höhe abgeschnitten werden. Die Einhaltung gleicher Schnitthöhe ist nämlich notwendig, weil die Analysenwerte, wie aus Tabelle VII ersichtlich ist, durch einen hohen Stengelanteil erniedrigt werden.

TABELLE VII

Schwermetallgehalte der Blätter und Stengel von <i>Trifolium pratense</i> der gleichen Probe					
Bodentyp	Pflanzenteil	Fe ppm	Mn ppm	Cu ppm	Co ppm
Podsol	Blätter u. Blüten. . .	96,7	41,2	8,81	0,039
	Stengel	29,8	13,5	4,90	0,017
Podsol	Blätter u. Blüten. . .	119,1	20,0	4,06	0,035
	Stengel	44,3	9,2	3,01	0,020
eutrophe	Blätter u. Blüten. . .	109,2	39,8	7,83	0,082
Braunerde	Stengel	26,3	11,6	3,90	0,025

Auch mit fortschreitender Entwicklung der Pflanzen ändern sich nach den Ergebnissen der Tabellen VIII bei *Trif. prat.* und IX beim Weidefutter die Schwermetallgehalte.

TABELLE VIII

Bodentyp	Erntedatum	Fe ppm	Mn ppm	Cu ppm	Co ppm
eutrophe Braunerde	1.5.1952	98,4	19,2	8,52	0,075
	5.5.1952	102,7	20,6	8,25	0,072
	12.5.1952	82,2	22,5	7,08	0,090
Humus- Gley- Podsol	1.5.1952	96,5	17,7	6,29	0,020
	12.5.1952	96,5	18,5	5,19	0,018
	23.5.1952	64,1	18,7	4,69	.

TABELLE IX

Bodentyp	Erntedatum	Weidefutter			
		Fe ppm	Mn ppm	Cu ppm	Co ppm
mesotrophe Braunerde	1.5.52	99,1	61,0	6,53	0,044
	5.5.52	121,8	47,8	6,89	0,076
	12.5.52	103,7	45,0	6,76	0,053
	23.5.52	101,5	44,4	5,55	0,039
Humus- Gley- Podsol	1.9.52	210,5	51,5	7,89	.
	5.5.52	94,4	57,8	6,99	0,014
	12.5.52	84,4	58,0	5,79	0,016
	23.5.52	59,1	57,2	4,99	0,018
	16.6.52	66,6	79,4	3,54	0,026

Um die durch die Pflanzenentwicklung bedingten Unterschiede möglichst zu vermeiden, wurde das Futter auf sämtlichen Standorten in der engen Zeitspanne zwischen dem Beginn des Schossens und der Blüte von *Lolium perenne*, das auf allen Weiden vorhanden war, geerntet. Untersucht wurde der erste Schnitt, da nach den Ergebnissen der Tabelle X verschiedene im vergleichbaren Entwicklungszustand von *Lol. per.* geerntete Schnitte ebenfalls unterschiedliche Schwermetallmengen enthalten.

TABELLE X

Erntezeitpunkt	Fe ppm	Mn ppm	Cu ppm	Co ppm
6.5.52	105,0	63,5	9,06	0,074
I. Schnitt				
30.5.52	78,4	51,9	6,01	0,082
II. Schnitt				

Durch den Gebrauch der Viehschere wurde die Gefahr, dass die Futterproben bei der Ernte durch Erde verunreinigt werden wesentlich herabgesetzt. Derartige Verunreinigungen müssen vermieden werden, da durch sie die Analysenwerte beeinflusst werden können. Das kommt am besten zum Ausdruck, wenn man in Tabelle XI die Konzentrationen der Schwermetalle in Böden und Pflanzen miteinander vergleicht. Es ergibt sich deutlich, dass die Kobaltanalysen auf dem Marschboden am stärksten beeinflusst werden können. Danach folgen mit grossem Abstand die anderen Standorte und Elemente.

TABELLE XI

Bodentyp	Probenmaterial	Fe ppm	Mn ppm	Cu ppm	Co ppm
Braunerde	Bodenprobe	1420	310	6,9	3,600
	Futterpr.	77	107	5,6	0,064
	Verhältnis Boden: Futter	18	2,9	1,2	56
Podsol	Bodenprobe	13	214	5,6	1,160
	Futterpr.	7	141	5,1	0,030
	Verhältnis Boden: Futter	12	1,5	1,1	39
Marschboden	Bodenprobe	125	417	11,6	7,300
	Futterpr.	7	111	5,9	0,044
	Verhältnis Boden: Futter	32	3,8	2,0	166
Niedermoor	Bodenprobe	1274	912	11,1	1,790
	Futterpr.	63	117	3,0	0,024
	Verhältnis Boden: Futter	20	7,8	3,7	75

Als Anhalt für etwaige Verunreinigung durch anhaftende Erde bestimmten wir in Anlehnung an Mitchell²⁰⁾ Eisen. Die verhältnismässig geringen Eisengehalte, die in Tabelle XII zusammengestellt wurden, lassen vermuten, dass die Futterproben nicht stark verunreinigt waren, so dass die gemessenen Kobaltwerte den wahren Gehalten zumindest sehr nahe kommen. Kobalt wäre wegen des weiten Konzentrationsverhältnisses Boden: Pflanze besser als Eisen als Indikator für Verunreinigungen geeignet. Da bisher die möglichen von Verunreinigungen unbeeinflussten Kobaltgehalte nicht ausreichend bekannt sind, scheidet es zunächst als Verunreinigungsindikator aus. Es besteht aber der Eindruck,

dass unter hiesigen Verhältnissen im jungen Weidefutter Werte über 0.1 ppm Kobalt stets die Folge von Verunreinigungen sind. Titan, das Mitchell als Verunreinigungsindikator bei spectrographischen Messungen empfiehlt, schied wegen Schwierigkeiten bei der photometrischen Bestimmung aus.

TABELLE XII

Fe ppm	Zahl der Proben	Fe ppm	v. H. der ge- samten Proben
—			
— 74	35	0— 74	28
75— 99	49	0— 99	67
100—124	33	0—124	93
125—149	5	0—149	97
mehr als 150	4		

Um Erde zu entfernen, die trotz sorgfältiger Probenahme den Futterpflanzen besonders nach Regenfällen anhaftet, wurden die frischen Pflanzenproben einmal in Leitungs- und anschliessend in destilliertem Wasser insgesamt höchstens 2 Minuten bei starker Bewegung gewaschen. Netzmittel, die Smith²⁸⁾ anwendet, wurden dem Wasser nicht zugesetzt. Die im Umlauftrockenschrank bei 100°C getrockneten Proben wurden im Starmix zerkleinert. Nach den bisherigen Ergebnissen ist nicht damit zu rechnen, dass das Pflanzenmaterial durch die aus poliertem Stahl gefertigten Messer des Starmix nachweisbar verunreinigt wird. Da der Mahlbecher aus Jenaer Glas besteht, sind Schwermetallverunreinigungen durch ihn ausgeschlossen.

Sämtliche *Bodenproben* wurden, soweit nicht ausdrücklich anders angegeben, aus 0–20 cm Tiefe gezogen. Hierbei wurden auf den 9 m² grossen Parzellen 20 Einstiche mit dem Bohrstock gemacht und die Bohrkerne zu einer Probe vereinigt. Für die Analysen wurde die Feinerde mittels eines Siebes mit 2 mm Maschenweite abgetrennt. Zur Bestimmung der Schwermetalle, der Kohlenstoff- und Stickstoffgehalte mahlten wir die Bodenproben in einer Porzellan-Kugelmühle staubfein. Hierdurch wurde die Einwaage einwandfreier Durchschnittsproben ermöglicht. Ausserdem benötigt man zum Aufschluss der gemahlenen Bodenprobe nur verhältnismässig wenig Flußsäure.

Die chemischen Analysenverfahren

Pflanzen- und Bodenproben wurden mit einem Gemisch aus Salpeter-, Perchlor- und Schwefelsäure im Kjeldahlkolben nass

verascht und die Kieselsäure mit Flußsäure abgeraucht. Die Behandlung der Pflanzenproben mit Flußsäure erwies sich als notwendig, da nach den Ergebnissen der Tabelle XIII Eisen, Mangan und Kupfer bei Abtrennung der Kieselsäure durch Filtration im Filtrerrückstand zurückgehalten werden.

TABELLE XIII

Probe	Flußsäurebehandlung	Stroh v. <i>Secale cereale</i>			
		Fe ppm	Mn ppm	Cu ppm	Co ppm
I	mit	38	24	4,5	0,022
	ohne.	33	23	4,1	0,023
	Fehler in %	—16	— 5	—16	+5
II	mit	28	22	4,3	0,029
	ohne.	27	20	4,0	0,028
	Fehler in %	— 4	— 9	— 5	—4

Verzichtet man bei der Bodenanalyse auf Aufschluss der Silikate mit Flußsäure, dann liegen die Kupfer- und Kobaltwerte durchschnittlich 15-20 Prozent unter den Gesamtgehalten. Die Analysenwerte der Mineralböden werden durch Flußsäureaufschluss stärker als die der Humusböden erhöht.

Sämtliche Schwermetalle wurden photometrisch nach Methoden bestimmt, die mit Ausnahme der Kupfermethode von S a n d e l ²⁴⁾ eingehend beschrieben werden.

Unmittelbar in der Aschenlösung bestimmten wir:

- Eisen mit *o*-Phenanthrolin nach Reduktion mit Hydrochinon,
- Mangan nach der Perjodatmethode,
- Kupfer mit Natriumdiäthylthiocarbamat.

Eisen, Mangan, Kobalt und Nickel wurden nach der Methode von Š e d i v e c u. V a š á k ²⁶⁾ durch Zusatz von Dinatriumäthylendiamintetraacetat (Komplexon III) maskiert.

Kobalt wurde zunächst mit Dithizon bei pH 8-8,5 abgetrennt und anschliessend mit *o*-Nitrosokresol (E l l i s und T h o m p s o n ⁶⁾) bestimmt. Diese Methode ist der Nitroso-R-Salz-Methode überlegen, da Fremdionen wie z.B. Kupfer die Messwerte nicht beeinflussen und das zur Lösung des Kobaltkomplexes benutzte organische Lösungsmittel (Petroläther) den Gebrauch von Küvetten mit relativ kleinem Querdurchmesser und damit grosser Schichtdicke bei geringer Lösungsmenge erlaubt. So benutzten wir Küvet-

ten mit 8.00 cm Schichtdicke, zu deren Füllung nur 7 cm Petroläther erforderlich waren. Die *o*-Nitrosokresol-Methode übertrifft das von Baron³⁾ zur Kobaltbestimmung empfohlene Verfahren mit β -Nitroso- α -naphthol durch mehrfache Empfindlichkeit.

In den Böden wurden ferner bestimmt:

- a) die pH-Werte in 1N KCl-Lösung mit der Chinhydronelektrode.
- b) Die Kohlenstoffgehalte durch Oxydation mit Kaliumbichromat (Methode L i c h t e r f e l d e).
- c) Gesamtstickstoff nach K j e l d a h l.

II. MANGANGEHALTE DES WEIDEFUTTERS UND DER BÖDEN

Das untersuchte Weidefutter enthielt, wie aus Tabelle XIV ersichtlich ist, zwischen 29 und 455 ppm Mangan. Die Schwankungsbreite der Mangangehalte aller Futterproben ist also verhältnismässig gross und wird von keinem der anderen untersuchten Schwermetalle, weder vom Eisen noch vom Kupfer oder Kobalt erreicht.

TABELLE XIV

Anzahl der Futterproben mit bestimmten Mangangehalten						
ppm Mn	29-90	91-180	181-270	271-360	361-450	455
Braunerden	9	1	2	—	—	—
Marschböden	1	2	1	1	—	—
Podsole, humusreich *)	8	6	5	3	—	1
Podsole, humusarm †)	6	2	—	—	—	—
Niedermoore	1	5	—	1	—	—
Insgesamt	25	16	8	5	—	1

*) mehr als 4,0% Kohlenstoff im lufttrockenen Boden.

†) weniger a. 4,0% Kohlenstoff im lufttrockenen Boden.

Unterschiedliche Mangangehalte wurden nicht nur im Futter auf Böden verschiedener Typengruppen sondern auch auf verschiedenen Böden der gleichen Typengruppe gemessen.

Nicht nur das Futter sondern auch die Böden unterscheiden sich, wie aus Tabelle XV abzulesen ist, durch ihre Mangangehalte erheblich voneinander. In diese Tabelle wurden die Mangangehalte in ppm und die Manganvorräte in kg/ha der 20 cm mächtigen

Krume eingetragen. Die durchschnittlichen Manganvorräte der Böden nehmen in der Reihenfolge Braunerden, Marschböden, Humus-Gley-Podsole, Niedermoores, humusreiche Podsole, humusarme Podsole ab.

TABELLE XV

Bodentyp	Zahl d. Proben	Mangangehalte und Manganvorräte					
		Maximalwert		Minimalwert		Durchschnittswert	
		ppm	kg/ha	ppm	kg/ha	ppm	kg/ha
Marschböden	5	559	1680	291	870	432	1290
Braunerden	12	626	1880	310	910	462	1380
Humus-Gley-Podsole	3	452	1130	419	1050	436	1090
Niedermoores	7	912	912	514	514	658	658
Podsole, humusreich *)	17	673	1550	64	150	247	568
Podsole, humusarm †)	7	214	540	78	190	132	330

*) Böden mit mehr als 4% Kohlenstoff.

†) Böden mit weniger als 4% Kohlenstoff.

Die untersuchten Podsole auf mitteldiluvialen Moränen, die auf der sogenannten alten Geest ostwärts anschliessend an die Marschböden verbreitet sind, enthalten durchschnittlich mehr Mangan als Podsole auf jungdiluvialen Sanden.

Die Unterschiede in den Mangangehalten verschiedener Böden werden besonders deutlich, wenn man Mangan in den einzelnen Horizonten einer mesotrophen Braunerde auf jungdiluvialen Geschiebemergel und eines starken Podsoles auf jungdiluvialen Sandersand bestimmt. Im C-Horizont der Braunerde wurde, wie aus Tabelle XVI ersichtlich ist, sechs mal so viel Mangan wie im gleichen Horizont des Podsoles gefunden.

TABELLE XVI

Horizont	Braunerde (pH 5,6)		Horizont	Podsol (pH 3,5)	
	Tiefe cm	Mn ppm		Mn ppm	Fe ppm
A	0-2	416	A ₀ + A ₁	30	697
	2-5	334	A ₂	36	860
	12-15	308			
(B)	45	246	B (Humusortstein)	68	1120
	50	158	B (Eisenortstein)	100	1820
C	85-90	431	C	69	1900

Im Gegensatz zur Braunerde ist aus den Analysendaten des Podsolprofils die nach unten gerichtete Manganverfrachtung abzulesen. Mangan wird hier in der Eisenortsteinlage angereichert.

Eine Beziehung zwischen den Manganvorräten der Böden einerseits und den Mangangehalten der Pflanzen andererseits besteht nicht. Das Futter der manganreichen Braunerden ist vielmehr durchschnittlich relativ manganarm.

Dies liegt in erster Linie an der nur schwach sauren Reaktion der meisten untersuchten Braunerden. Es ist nämlich eine bekannte Tatsache ^{8) 11) 17)}, dass Pflanzen bei tiefen pH-Werten relativ viel Mangan aufzunehmen vermögen. Dieser Zusammenhang zwischen Bodenreaktion und Mangangehalt des Futters kommt auch in Tabelle XVII zum Ausdruck.

TABELLE XVII

Bodentyp	pH-Werte der Böden		Mangangehalte d. Futters (ppm)	
	von	bis	von	bis
Braunerden	5,2	6,1	107	29
Marschböden	4,8	7,7	344	58
Podsole 4% C.	4,7	6,9	141	38
Podsole 4% C.	3,5	6,3	455	49
Humus-Gley-Podsole	5,3	5,8	79	59
Niedermoore	4,8	5,7	332	81

Je stärker die pH-Werte der Böden von einander abweichen, desto grösser sind die Unterschiede in den Mangangehalten der Pflanzen.

Besonders deutlich war der Einfluss der Bodenreaktion in den Mangangehalten des Futters zweier Parzellen zu erkennen, die beiderseits eines gemeinsamen Koppelzaunes auf der gleichen Weide angelegt waren. Bedingt durch langjährige unterschiedliche Düngung betrugen die pH-Werte bei der einen 3.5, bei der anderen Parzelle 4.2. Das Futter der entsprechenden Parzellen enthielt 259 bzw. 96 ppm Mangan.

Der Mangangehalt der Pflanzen ist auf Böden verschiedener Typengruppen aber nicht im gleichen Umfang vom pH-Wert abhängig. Beispielsweise enthielt bei pH etwa 5.2 das Futter auf einer Braunerde 32 ppm, auf einem humusarmen Podsol 192 ppm Mangan. Bei pH etwa 6 waren im allgemeinen die Mangangehalte

im Futter aller dieser Böden verhältnismässig ausgeglichen und lagen zwischen 30 und 60 ppm.

Eine Ausnahme machen einige Marschböden, auf denen die Futterpflanzen auch bei pH-Werten um 6 relativ viel Mangan, nämlich bei pH 5.8 343 ppm und bei pH 6.9 260 ppm enthielten.

Diskussion

Mangan wird von den Pflanzen als Mn^{II} -Ion, möglicherweise ausserdem nach Mattson¹⁶⁾ als Mn^{III} -Pyrophosphat aufgenommen. Da Mangan im Boden hauptsächlich in Oxyd-Form vorliegt, kann die Pflanze um so mehr Mangan aufnehmen, je stärker die reduzierenden Bedingungen im Boden sind. Reduktionsvorgänge laufen im Boden um so schneller ab, je tiefer sein pH-Wert und je höher sein Gehalt an leichtoxydierbaren organischen Substanzen ist. Derartige Verhältnisse findet man in sauren, humusreichen Podsolen mit weiten C : N-Verhältnissen. Das Futter dieser Böden enthält daher besonders viel Mangan. Demgegenüber stellen die meisten Braunerden den Pflanzen relativ wenig Mangan zur Verfügung. Verständlich wird dies Ergebnis, wenn man berücksichtigt, dass Braunerden relativ wenig reduzierende organische Substanzen enthalten. Die Humusstoffe dieser Böden sind nämlich ausgereift und sauerstoffgesättigt. Die relativ hohen Mangangehalte im Futter einiger Marschböden sind durch die reduzierenden Bedingungen in diesen Böden mit Gley-Horizonten zu erklären.

III. KUPFERGEHALTE DES WEIDEFUTTERS UND DER BÖDEN

Da in Schleswig-Holstein Kupfermangel der Kulturpflanzen und des Viehs nur auf Podsolen und Niedermooren der Geest aufgetreten ist, wurde vermutet, dass das Futter auf diesen Böden verhältnismässig wenig Kupfer enthält. Diese Vermutung hat sich, wie aus Figur 1 ersichtlich ist, bestätigt. Geringe Kupfermengen unter 5 ppm fanden wir nämlich nur im Futter auf Podsolen und Niedermooren.

Diese Böden sind gegenüber Braunerden und Marschböden ebenfalls kupferarm. Der geringe Kupfergehalt der Podsole wird besonders deutlich, wenn man in Tabelle XVIII die Verteilung des Kupfers in verschiedenen Horizonten einer mesotrophen Braunerde (Weide) und eines starken Podsols (Ödland, vorherrschend *Calluna*

vulgaris) betrachtet. Die einzelnen Horizonte der Braunerde enthalten etwa doppelt so viel Kupfer wie die des Podsoles, in dessen humusreicheren $A_0 + A_1$ -Horizonten Kupfer angereichert ist. Der hohe Kupfergehalt der obersten Bodenlagen muss durch die Pump-

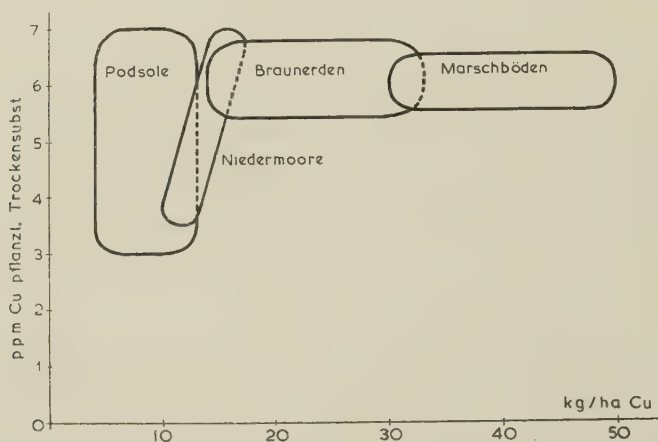


Fig. 1. Kupfergehalte der Pflanzen und Kupfervorräte der Böden.

leistung der Vegetation erklärt werden, zumal *Calluna vulgaris* auf einem ähnlichen Standort 5.1 ppm Kupfer enthielt, also relativ kupferreich war. Eine unter dem Einfluss der Podsolierung abwärts gerichtete Verfrachtung von Kupfer ist aus den Ergebnissen der Tabelle XVIII nicht abzulesen.

TABELLE XVIII

Horizont	Braunerde		Horizont	Podsol Cu ppm
	Tiefe	Cu ppm		
A	0-2	10,7	$A_0 + A_1$	5,3
	2-5	10,0	A_2	2,7
	12-15	9,1		
(B)	45	10,4	B (Humusortstein)	4,7
	50	6,8	B (Eisenortstein)	4,1
C	85-90	11,8	C	4,0

Aus Figur 1 ergibt sich keine eindeutige Beziehung zwischen den Kupfervorräten der Böden einerseits und den Kupfergehalten der Pflanzen andererseits. Geringe Kupferkonzentrationen unter 5 ppm

wurden aber nur im Futter von Böden gemessen, die wie Podsole und Niedermoore wenig Kupfer enthalten.

Die unzureichende Versorgung der Pflanzen mit Kupfer auf manchen Podsolen und Niedermooren wird auf Fixierung (S t e e n b j e r g ²⁹⁾), möglicherweise durch bestimmte Humusstoffe (H o f f m a n n ¹³⁾), geschoben. Ein Nährstoff ist fixiert und damit für die Pflanzen nicht oder nur in geringem Ausmass verfügbar, wenn die Pflanzen nur einen geringen Anteil vom gesamten Nährstoffvorrat des Bodens aufzunehmen vermögen. Unter bestimmten Voraussetzungen — gleiche Erträge innerhalb gleicher Wachstumszeit, gleiche Wurzeleistung — liesse sich die „Pflanzenverfügbarkeit“ eines Nährelementes aus den Nährelementkonzentrationen in Pflanze und Boden berechnen, sofern das Angebot das Fassungsvermögen der Pflanzen nicht wesentlich überschreitet.

Obgleich diese Voraussetzungen beim Untersuchungsmaterial der vorliegenden Arbeit nicht erfüllt sind, wurden die Relationswerte in Tabelle XIX als Anhaltswert für die Verfügbarkeit nach der Formel

$$\frac{N_{(\text{Pflanze})} \cdot 100}{N_{(\text{Boden})} \cdot \text{Raumgewicht d. Bodens}}$$

errechnet.

TABELLE XIX

	Kupfer (Mittelwerte)	Kobalt (Mittelwerte)
Marschböden	32	0,6
Braunerden	55	0,9
Niedermoore	78	2,0
Podsole	118	3,4

Aus den Relationswerten — die nach dem Vorhergesagten nur mit Vorbehalt auszuwerten sind — ergibt sich eine bessere Verfügbarkeit des Bodenkupfers auf Böden mit höherem Humusgehalt.

Zwischen den Kupfergehalten der Pflanzen und den pH-Werten der Böden besteht im Gegensatz zu ihrem Mangangehalt keine deutliche Beziehung. Diese Tatsache war sowohl aus den Futteranalysen als aus den Ergebnissen eines Gefässversuches mit Senf (Tabelle XX) abzulesen.

TABELLE XX

Düngung			Ertrag je Gefäss g	pH KCl	Mangan		Kupfer	
Ca	Cu	Mn			Gehalt d. Pflanze ppm	Entzug je Gefäss %	Gehalt d. Pflanze ppm	Entzug je Gefäss %
—	—	—	0,52	4,0	313	163	12,8	6,7
—	+	+	0,49	4,0	417	204	15,6	7,6
I	—	—	2,9	5,3	24	70	9,0	26
I	+	+	4,5	5,3	34	153	9,7	44
II	—	—	5,0	6,1	24	121	11,3	51
II	+	+	5,2	6,1	31	162	10,9	57

Düngung: Ca I = 59,5 dz/ha CaO als Mischkalk.

Ca II = 122,5 „ „ „ „ „

Cu = 100 kg/ha Kupfersulfat.

Mn = 100 kg/ha Mangansulfat.

Der Senf war in den nicht gekalkten Gefässen in seiner Entwicklung stark gehemmt. Bereits durch die einfache Kalkgabe wurden die Pflanzen wesentlich gefördert. Als Folge der Kalkung ist die Pflanzenverfügbarkeit des Mangans und damit der Mangan-gehalt der Pflanzen stark zurückgegangen, so dass der Mangan-entzug trotz höherer Erträge unter den der ungekalkten Gefässe abge-sunken ist. Ein derartiger Einfluss der Reaktionsverschiebung auf die Kupfergehalte ist nicht abzulesen.

Diskussion

Aus einem Vergleich der Relationswerte der Podsol- und Nieder-moorstandorte einerseits und der Braunerden- und Marschboden-standorte andererseits ergibt sich, dass das Weidefutter auf Pod-solen und Niedermooren verhältnismässig viel Kupfer aufzunehmen vermag.

Die Untersuchungsergebnisse von Hoffmann¹³⁾ und Steenbjerg²⁹⁾, nach denen eine besonders starke Fixierung des Kupfers als Ursache für die häufig unzureichende Kupferver-sorgung der Pflanzen auf einigen Podsolen und Niedermooren ange-sehen wird, gelten für die in dieser Arbeit untersuchten Standorte nicht. Es besteht vielmehr der Eindruck, dass das Futter mancher untersuchter Podsole und Niedermoore deshalb kupferarm ist, weil die Böden selbst nur geringe Kupfervorräte enthalten. Und zwar enthalten sie 25–30 kg/ha Kupfer weniger als Marschböden, 15–20 kg/ha weniger als Braunerden.

Auf allen Böden mit mehr als 20 kg/ha Kupfer wurden im Weide-

futter mehr als 5 ppm Kupfer gemessen. Zu ähnlichen Ergebnissen kamen Lundblad und Mitarbeiter¹⁶⁾.

Aus den Kupferanalysen des Podsolprofils ist eine Anreicherung von Kupfer in den humusreichen $A_0 + A_1$ -Horizonten abzulesen. Eine Abwärtsverfrachtung von Kupfer ist nicht zu erkennen. Sie wäre nicht gegeben, wenn die als C-Horizont bezeichnete Lage tatsächlich ein echter C-Horizont, also frei von Verlagerungen wäre.

IV. KOBALTGEHALTE DES WEIDEFUTTERS UND DER BÖDEN

In Figur 2 wurden die Kobaltgehalte des Futters und die Kobaltvorräte der Böden zueinander in Beziehung gesetzt. Man erkennt die Tendenz einer Abhängigkeit der Kobaltgehalte des Futters von den Kobaltvorräten der Böden. Dieser Zusammenhang ist aus den Analysenwerten der Böden der einzelnen Typengruppen, von den Niedermooren abgesehen, nicht zu erkennen.

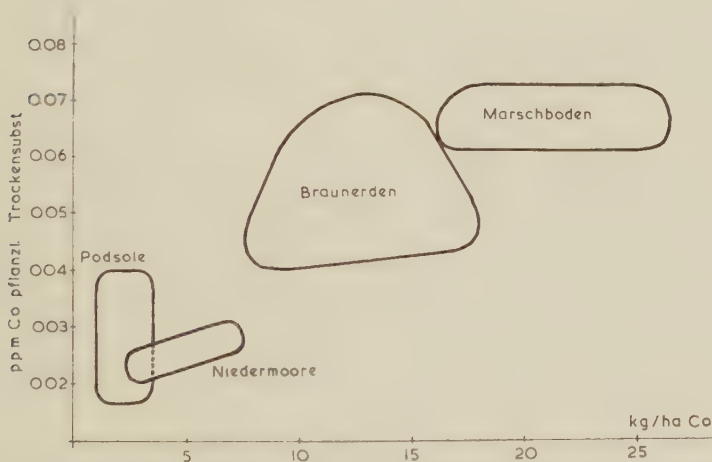


Fig. 2. Kobaltgehalte der Pflanzen und Kobaltvorräte der Böden.

Während das Futter der Marschböden und Braunerden verhältnismässig kobaltreich ist, müssen die auf den untersuchten Podsolon und Niedermooren gezogenen Futterproben, die sämtlich weniger als 0.04 ppm Kobalt enthalten, im Hinblick auf die Kobaltversorgung der Weidetiere nach Literaturangaben^{4) 30)} mög-

licherweise als kobaltarm angesprochen werden. Auf den Podsolen ist nicht nur das Weidefutter, sondern wie aus Tabelle XXI ersichtlich ist, auch das zur Heugewinnung angebaute Gemenge aus *Trifolium prat.* und *Lolium per.* verhältnismässig arm an Kobalt.

TABELLE XXI

Bodentyp	Pflanzenart	Zahl d. Proben	Kobaltgehalt		
			Maximal Wert ppm	Minimal Wert ppm	Durchschn. Wert ppm
Podsolboden	<i>Trifolium prat.</i>	7	0,040	0,020	0,029
	<i>Lolium per.</i>	7	0,027	0,018	0,021
Braunerde	<i>Trifolium prat.</i>	7	0,150	0,032	0,071
	<i>Lolium per.</i>	4	0,078	0,025	0,044

Vergleicht man in Tabelle XXII und Figur 2 die Kobaltgehalte von Böden verschiedener Typengruppen, so fällt auf, dass die untersuchten Böden um so kobaltreicher sind, je grösser ihr Tongehalt ist. Die Tongehalte nehmen nämlich in der Reihenfolge Podsole, Braunerden, Marschböden zu. Diese Feststellung gilt auch für Böden der gleichen Typengruppe mit unterschiedlichem Tonanteil. Die untersuchten Niedermoore in der Zone der Braunerden enthielten 2–3 mal so viel Kobalt wie solche in der Podsolzone.

TABELLE XXII

Mesotrophe Braunerde				Starker Podsol		
Horizont	Tiefe cm	Bodenart	Co ppm	Horizont	Bodenart	Co ppm
A	0– 2	sL *)	2,27	A ₀ + A ₁	S	0,28
	2– 5	sL	3,16	A ₂	S	0,22
	12–15	sL	3,44			
(B)	45	sL	3,95	B (Humusortstein)	S	0,42
	50	S †)	2,74	B (Eisenortstein)	S	0,44
C	85–90	Kies	5,10	C	S	0,53

*) sandiger Lehm.

†) Sand.

Trotz der Tätigkeit der Vegetation wird Kobalt wie Mangan und Eisen (siehe Tabelle XVI) im sauren Podsol (pH 3.5) abwärts verfrachtet. Auf einem ähnlichen Standort enthielten die jungen Triebe von *Calluna vulg.* 0.14 ppm Kobalt obgleich der Boden nur 0.16 ppm besass.

Die bei saurer Reaktion relativ hohe Löslichkeit von Kobalt im Boden ergibt sich auch aus den Werten der Tabelle XXIII.

Bei diesem Versuch wurde ein humusreicher Podsol in Mitscherlichgefässen nach Hafer mit 1 l Regenwasser (pH 6.5) durchgewaschen. Die Schwermetalle wurden in 300 ml des Waschwassers bestimmt.

TABELLE XXIII

pH des Bodens vor dem Auswaschen	Düngung			Co im Waschwasser	Cu im Waschwasser
	Ca	Cu	Gründünger	γ	γ
4,65	—	—	—	3,9	1,2
6,49	I	—	—	3,3	2,6
6,60	II	—	—	1,5	—
4,55	—	+	—	3,2	1,9
6,38	I	+	—	4,5	3,2
7,03	II	+	—	1,5	4,9
4,57	—	+	+	4,3	2,3
6,67	I	+	+	1,1	6,9
7,15	II	+	+	0,8	5,2

Anm.: Düngung: Ca I = 61 dz ha CaO als Mischkalk.

Ca II = 90 „ „ „ „ „ „

Cu = 100 kg/ha Kupfersulfat.

Gründünger: Serradella.

Im Gegensatz zum Kupfer, das in den Waschwässern der gekalkten Gefässe angereichert war, ist die Kobaltkonzentration nach der Kalkung geringer geworden.

Die Abhängigkeit der Löslichkeit des Kobalts von der Bodenreaktion macht sich auch in den Kobaltgehalten der Pflanzen bemerkbar. Denn bei relativ tiefen pH-Werten enthielt das Futter durchschnittlich etwas grössere Kobaltmengen. Die Beziehung zwischen den Bodenreaktionen und Kobaltgehalten der Pflanzen ist aber nicht so deutlich wie bei den Mangangehalten ausgeprägt. Nur im Gefässversuch der Tabelle XXIV zeigt sich eine stärkere Abhängigkeit des Kobaltgehaltes von Senf von dem pH-Wert des Bodens.

TABELLE XXIV

		Mittelwerte von 4 Gefässen mit Senf			
pH	Ertrag g	Kobalt		Mangan	Kupfer
		ppm	Entzug γ	Entzug γ	Entzug γ
4,2	3,2	1,16	3,7	784	27
6,0	6,1	0,47	2,9	329	42
6,3	7,2	0,55	4,0	381	35
6,4	8,8	0,23	2,0	475	53
6,6	7,7	0,45	3,5	384	51

Die Kobaltgehalte nehmen mit steigendem pH-Wert so stark ab, dass die Kobaltentzüge trotz steigender Erträge nahezu unverändert geblieben, teilweise sogar abgesunken sind. Noch deutlicher ist eine Festlegung beim Mangan ausgeprägt während im Gegensatz hierzu die Kupferentzüge mit den Erträgen angestiegen sind. Auffälligerweise enthält der Senf in den Gefäßen 10 mal so viel Kobalt wie das Weidefutter auf natürlichen Standorten.

Bemerkenswert ist die Tatsache, dass auf sämtlichen untersuchten Standorten Kobalt verglichen mit Mangan und Kupfer nur in geringen Mengen für die Pflanzen aufnehmbar ist. Denn während die Böden durchschnittlich etwa bis 6 mal so viel Kupfer wie Kobalt enthielten, wurden in den Pflanzen, wie aus Tabelle XXV ersichtlich ist, allgemein Kupfer:Kobalt-Verhältnisse von 100–200 : 1 gemessen.

TABELLE XXV

Mengenverhältnisse der Schwermetalle Kupfer und Kobalt in Pflanzen und Böden						
Bodentyp	Weidefutter			Boden		
	Cu ppm	Co ppm	Cu : Co	Cu ppm	Co ppm	Cu : Co
Braunerde	5,6	0,064	87	6,9	3,60	1,9
Marschboden	5,9	0,044	136	11,6	7,30	1,6
Podsol	3,4	0,017	202	3,3	0,96	3,4
Niedermoor	3,0	0,024	127	11,1	1,79	6,2

Die Relationswerte des Kobalts liegen daher, wie aus Tabelle XIX abzulesen war, unter denen des Kupfers.

Diskussion

Sowohl aus Untersuchungen von Mitchell²⁰⁾ und Ekman⁵⁾ als auch aus den eigenen Analysendaten geht hervor, dass die Kobaltgehalte der Pflanzen bei höheren pH-Werten der Böden absinken. Die zwischen Braunerden und Marschböden einerseits und Podsolen und Niedermooren andererseits ermittelte unterschiedliche Verfügbarkeit des Kobalts ist durch Reaktionseinflüsse nicht zu erklären. Sie beruht möglicherweise auf einer Festlegung grosser Teile des Kobalts im Kristallgitter der Silikate (Schierbold²⁵⁾, Mitchell²⁰⁾), an denen die untersuchten Braunerden und Marschböden verglichen mit Podsolen reich sind.

Gegenüber Kupfer und Mangan ist Kobalt für die Pflanzen besonders schlecht verfügbar. Der Mechanismus der Fixierung ist

bisher nicht bekannt. Vielleicht beruht die geringe Verfügbarkeit des Kobalts auf seiner im Vergleich zu anderen Kationen relativ starken Bindung an organische und anorganische Bodenaustauscher. (Banerjee²⁷), Heinze und Mann¹²). Ausserdem besitzen niedere Organismen teilweise die Fähigkeit zu starker Konzentrierung von Kobalt (Lange de la Camp¹⁵), so dass auch an biologische Festlegung zu denken wäre.

ZUSAMMENFASSUNG

1. Mangan-, Kupfer- und Kobaltgehalte wurden im Weidefutter und Böden von 30 Podsol-, 14 Braunerde-, 7 Niedermoor- und 5 Marschbodenstandorten bestimmt.

2. Die Schwermetallgehalte des Futters weichen auf verschiedenen Weiden erheblich voneinander ab. Sie werden vom Boden, dem Erntezeitpunkt und der botanischen Zusammensetzung des Futters beeinflusst.

3. Die mittleren Mangangehalte des Futters verschiedener Bodentypen nehmen in der Reihenfolge Podsole, Marschböden, Niedermoore, Braunerden ab.

4. Der pflanzenverfügbare Mangananteil und damit der Mangangehalt des Futters sinkt mit steigendem pH-Wert des Bodens. Unterschiede in der Bodenreaktion beeinflussen die Schwankungsbreite der Mangangehalte des Futters auf Podsolen und Niedermooeren stärker als auf Braunerden.

5. Braunerden und Marschböden, die durchschnittlich 1200–1400 kg/ha Mangan enthalten, sind verglichen mit Podsol- und Niedermoorböden, deren Manganvorräte 400–700 kg/ha betragen, manganreich. Mangan wurde im untersuchten Podsol abwärts verfrachtet und im B-Horizont angereichert.

6. Auf Braunerde- und Marschbodenstandorten enthält das Weidefutter 5.6–9.0 ppm Kupfer, auf Podsolen 3.2–7.1 ppm, auf Niedermooeren 3.0–7.6 ppm.

7. Die Kupfervorräte der Böden nehmen in der Reihenfolge Marschböden (48–28 kg/ha), Braunerden (43–19 kg/ha), Niedermoore (16–11 kg/ha), Podsole (16–4 kg/ha) ab. An einem untersuchten Podsolprofil enthielten $A_0 + A_1$ relativ viel Kupfer.

8. Auf sämtlichen Mineralbodenstandorten mit mehr als 20 kg/ha Kupfer war im Futter mehr als 5 ppm Kupfer vorhanden.

9. Beziehung zwischen dem Humusgehalt, dem Kohlenstoff:Stickstoff-Verhältnis und dem pH-Wert des Bodens einerseits, dem Kupfergehalt des Weidefutters andererseits sind nicht erkennbar.

10. Die Kobaltgehalte des Weidefutters verschiedener Standorte nehmen in der Reihenfolge Marschböden (0.075–0.044 ppm), Braunerden (0.074–0.029 ppm), Podsole (0.056–0.017 ppm), Niedermoore (0.036–0.022 ppm) ab.

11. In der gleichen Reihenfolge nehmen die Kobaltvorräte der Böden ab. Es enthalten nämlich Marschböden 26–18 kg/ha, Braunerden 19–9 kg/ha, Niedermoore 7–2 kg/ha, Podsole 4–1 kg/ha. Am Profil eines Podsols ist die Abwärtsverfrachtung von Kobalt meßbar.

Die Untersuchung wurde durch eine Forschungsbeihilfe ermöglicht, die das Bundesministerium für Ernährung, Landwirtschaft und Forsten aus E R P-Mitteln dankenswerterweise zur Verfügung gestellt hatte. Herrn Prof. Dr. Laatsch danke ich für sein Interesse, das er der Arbeit entgegengebracht hat und für seine fachlichen Hinweise. Herr Prof. Dr. Köhnlein überließ mir freundlicherweise einiges Versuchsmaterial zur Auswertung. Fräulein Ingeburg Kämmerling unterstützte mich dankenswerterweise bei den Schwermetallanalysen.

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CONDUCTIVITY OF SOIL-WATER EXTRACT AS AN INDEX OF SOIL STRUCTURE *)

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INTRODUCTION

In reports on lysimeter studies¹ it has been observed that the rise in specific conductance of the leachings was associated with seasonal mobilization of electrolytes, chiefly alkalies and alkaline earths, particularly during the fall season. It was then postulated that these electrolytes promote coagulation of colloids which in turn favors non-capillary pore space and hence greater percolation. Since percolation is a good index of the state of aggregation in soils it was assumed that the structure had improved. However, no direct evidence has been forthcoming on the relation of electrolytes as expressed by specific conductance and soil structure. The object of this paper is to present such evidence.

EXPERIMENTAL AND DISCUSSION OF RESULTS

The parent material of soils studied (Farm of the National Agricultural College, Farm School, Pennsylvania) consists of arkose, stratified sandstone rock, made up chiefly of feldspars, quartz, and micas. This soil is classified as Chester loam. Pedologically it belongs to the Gray-Brown Podzolic group.

Five profiles from different cropping systems were sampled monthly (with the exception of January, 1952) beginning with August, 1950, through May, 1952. The samples were: surface of Ap, 0-3"; bottom of Ap, 4-6"; A₂ horizon, 10-12"; B horizon, 14-18" depth.

*) Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, Department of Soils.

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The cropping systems of the profiles sampled were: Profile No. 1 had corn in summer and spinach in fall of 1950; carrots in 1951; fallow in the fall and winter of 1951; and corn in 1952. Profile 2 had rye in 1950, winter wheat in 1950-1951, with hay from summer of 1951 through the spring of 1952. Profile 3 was in pasture through 1950-1952. Profile 4 was fallow through 1950-1952. Profile 5 was in meadow through 1950-1952.

Mechanical analyses of the soil studied, Table I, show profile 1 containing more silt and clay than the other profiles. This did not result in better structure for this profile, as shown in Table II. Variations in structure in the five profiles may be accounted for in some

TABLE I

Mechanical analyses of five profiles used to measure seasonal variations in structure			
Horizon	Sand per cent	Silt per cent	Clay per cent
<i>Profile 1</i>			
Ap (top)	33.4	44.2	22.4
Ap (bottom)	26.4	43.2	30.4
A ₂	24.4	41.0	34.6
B	29.4	36.2	34.4
<i>Profile 2</i>			
Ap (top)	46.4	33.2	20.4
Ap (bottom)	42.4	36.2	21.4
A ₂	44.4	32.2	23.4
B	31.4	37.2	31.4
<i>Profile 3</i>			
Ap (top)	51.4	30.2	18.4
Ap (bottom)	53.4	28.2	18.4
A ₂	52.4	28.2	19.4
B	52.4	23.2	24.4
<i>Profile 4</i>			
Ap (top)	51.4	25.2	23.4
Ap (bottom)	51.4	25.2	23.4
A ₂	58.4	18.2	23.4
B	59.4	16.2	24.4
<i>Profile 5</i>			
Ap (top)	52.4	26.2	21.4
Ap (bottom)	51.4	26.2	22.4
A ₂	52.4	24.2	23.4
B	56.4	22.2	21.4

TABLE II
Seasonal variations of soil structure in horizons of five profiles reported as structural index

Horizon	Sampling period																			
	1950					1951					1952									
	8/10	8/31	10/3	11/10	12/18	1/19	2/27	3/27	4/24	5/8	5/28	6/18	7/9	8/3	9/5	10/4	11/13	12/24	2/6	3/17
<i>Profile 1</i>																				
Ap (top)	1	2	1	1	1	1	1	1	1	1	1	2	1	2	1	2	3	2	1	1
Ap (bot.)	2	3	2	2	3	1	1	1	1	2	1.5	1	2	1	1	1	2	2	1	2
A ₂	1	1	1.5	2	1.5	1	1.5	1	2	1	2	1	1	1	1	1	2	2	1	1
B	1	1	1.5	2	2	1	1.5	2	2	1	2	2	1	1	1	1	2	2	2	1
<i>Profile 2</i>																				
Ap (top)	1	2	1	1	2	1	1	2	1.5	1.5	2	2	1.5	2	3	2	2	2	2	1
Ap (bot.)	1	1	1.5	2	2	1	1	1	1	1	1	1	1.5	1.5	1	1	1	2	2	1
A ₂	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
B	1	1	1	2.5	2	1	1.5	1.5	1	1	1	1	1	1	1	1	1	1	1	1
<i>Profile 3</i>																				
Ap (top)	1.5	2	2.5	2.5	3	3	2.5	2.5	2.5	3	3	3	3	3	3	3	3	3	1	3
Ap (bot.)	2.5	2.5	1.5	2	1	3	3	2	1.5	2	2	1	3	3	1	2.5	2	3	1	1
A ₂	1	1.5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
B	1.5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
<i>Profile 4</i>																				
Ap (top)	1.5	2.5	2.5	3	2.5	2	1	1	1	1	1	1	1	2	2	2	3	2	3	1
Ap (bot.)	1	2.5	2	3	1.5	1	1	1	1	1	1	2	1	2	1	1	1	2	2	1
A ₂	2	1	1	1	1	2	1	1	1	1	1	1	1	1	1	1	2	1	1	1
B	2	1	1	1	1	1.5	2	1	1	1	1	1	1	1	1	1	1	1	1	1
<i>Profile 5</i>																				
Ap (top)	2	1	2.5	2	2	1.5	1.5	1.5	1.5	1	1.5	2.5	3	3	3	3	3	2	2	3
Ap (bot.)	2.5	1	2.5	2	1.5	2	2	2	1	2	2	2	3	2	3	2	3	1	1	2
A ₂	1	1.5	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
B	1	1	1	1.5	1	1.5	1	1.5	1	1	1	1	1	1	1	1	1	1	1	1
Aver.	1.4	1.5	1.5	1.7	1.6	1.4	1.4	1.3	1.3	1.3	1.4	1.5	1.5	1.6	1.5	1.5	1.8	1.7	1.4	1.3

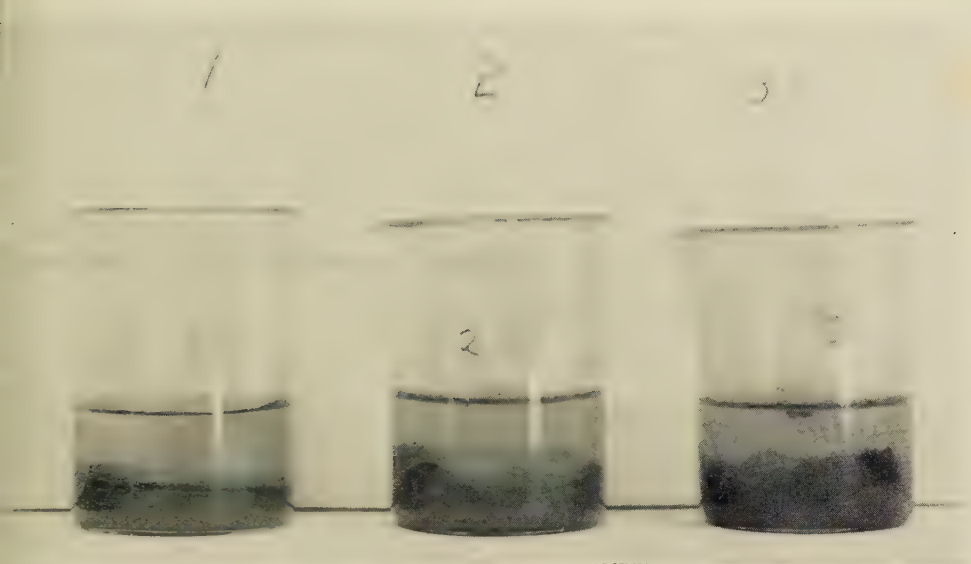


Plate I. Structural index of samples of Chester loam after wetting.

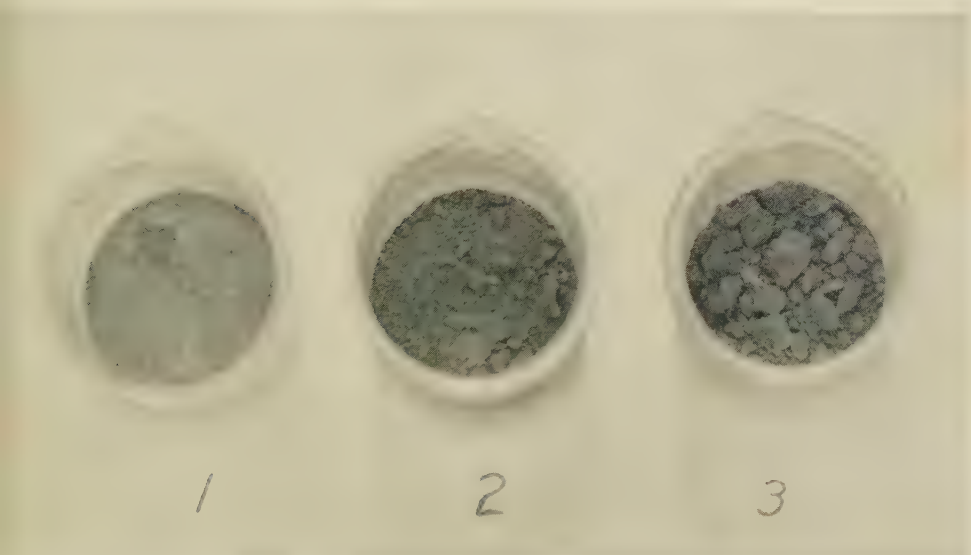


Plate II. Structural index of samples of Chester loam after drying.

cases by differences in cropping systems, in others by the type of electrolytes, or droughty or wet conditions. However, these variations are not clear cut and are subordinated to the direct relationship between the specific conductance and structure conditions, as shown presently.

Structure was evaluated by the method developed by the senior author more than 15 years ago. It consists of immersing about a 25-gram clod of soil at field moisture into 100 ml beaker containing 50 ml of water and allowing it to slake. The slaking action, from mud to various degrees of granulation, designated by the empirical values of 3, 2, 1 (in descending order of granulation), is recorded after 20–30 minutes. This method is simple and fast. Results are more accurately reproducible and more reassuring than those obtained by cumbersome wet or dry sieve methods. The excess water is siphoned off and the soil allowed to dry at room temperature.

Plate I, upon close examination, shows the variation in granulation after slaking. The decreased volume of the soil poorest in structure (No. 1) is obvious. Plate II shows clearly the difference in structure after drying. The soil with poorest structure (No. 1) showed a hard crust and dense constitution. This sample also showed resistance when a metal point was pressed into it. The values for the wet soil and for the dry soil were averaged and reported in Table II as structural index.

Air-dried samples of these soils were passed through a 2-mm screen and 50 grams mixed with 150 ml of distilled water, shaken at intervals over a period of 10 minutes, filtered and specific conductance determined and recorded in $\text{mhos} \times 10^5$. The results are given in Table III.

The data were analyzed statistically. They show significant seasonal differences in structure and conductivity (determined by the method of analysis of variance) and a positive correlation between seasonal differences in structure and seasonal differences in conductivity (determined by analysis of covariance). These data are summarized as the averages for each season in Table IV.

Figure 1 presents summation curves of nitrates, structure, and specific conductance; each point (21 in all) on the curves represents an average of 20 samples (4 horizon depths for each one of the 5 profiles), plotted as functions of time over a period of close to 2 years; in all an average of 420 samples (20×21).

TABLE III

Horizon	Seasonal variations of soil conductivity in horizons of five profiles reported as mhos $\times 10^5$																			
	1950										1951									
	Sampling period										Sampling period									
	8/10	8/31	10/3	11/10	12/18	1/19	2/27	3/27	4/24	5/8	5/28	6/18	7/9	8/3	9/5	10/4	11/13	12/24	2/6	3/17
<i>Profile 1</i>																				
Ap (top)	6	14	11	19	11	11	6	7	5	4	8	4	5	5	5	5	20	4	4	5
Ap (bot.)	8	7	7	15	13	13	6	7	5	5	7	4	4	4	6	6	6	4	3	5
A ₂	6	5	6	10	14	16	8	9	6	4	7	5	5	5	4	5	8	4	5	5
B	5	4	4	8	13	14	9	8	6	6	6	5	6	5	5	5	9	5	5	7
<i>Profile 2</i>																				
Ap (top)	7	4	7	15	7	12	5	5	4	5	4	4	6	6	8	5	5	6	5	5
Ap (bot.)	5	3	6	10	5	9	3	4	3	3	4	3	5	5	5	4	6	4	3	4
A ₂	4	2	6	7	11	11	4	5	3	3	3	3	4	4	4	3	8	4	3	4
B	3	3	6	6	8	11	5	4	4	4	4	3	4	4	4	4	5	5	3	4
<i>Profile 3</i>																				
Ap (top)	2	3	5	6	6	8	5	4	3	4	4	5	6	8	39	17	14	6	4	4
Ap (bot.)	2	2	4	5	7	7	4	4	3	3	3	3	4	4	14	14	18	5	3	4
A ₂	3	2	4	4	7	5	4	3	2	2	3	3	4	4	7	4	7	9	3	3
B	3	2	4	4	5	7	6	4	3	3	4	3	5	3	7	4	6	6	3	4
<i>Profile 4</i>																				
Ap (top)	11	9	24	6	5	7	4	4	5	5	5	5	5	7	10	13	5	5	3	4
Ap (bot.)	12	9	16	7	6	7	4	4	4	4	5	5	5	8	7	7	6	5	3	4
A ₂	7	4	10	8	10	8	6	5	4	4	4	4	5	5	4	5	10	5	3	4
B	10	4	5	8	7	9	5	5	4	4	3	4	6	5	5	5	9	4	4	4
<i>Profile 5</i>																				
Ap (top)	4	4	5	4	3	8	4	3	4	2	3	4	8	4	4	6	5	5	3	3
Ap (bot.)	4	3	3	4	4	4	5	4	3	2	2	4	8	3	3	3	5	2	2	3
A ₂	4	3	4	3	9	4	5	4	4	3	3	4	4	3	5	4	4	3	2	3
B	4	4	4	4	7	5	6	4	5	4	3	3	4	4	5	3	5	3	3	4
Aver.	5.5	4.6	7.1	7.7	7.9	8.8	5.7	4.9	4.0	3.7	4.3	3.9	5.3	4.8	7.6	6.0	8.0	4.7	3.4	3.9

TABLE IV

Season	Structure	Conductivity mhos $\times 10^5$
Spring	1.36	4.0
Summer	1.50	5.8
Fall	1.62	7.4
Winter	1.36	4.6

The curves on specific conductance and structure are almost identical. Such a close relationship between two important elements of soil conditions, the physical (structure) and the chemical (specific conductance), is highly significant. It would appear that specific conductance is an excellent yardstick for measuring the seasonal dynamics of soil structure in the gray-brown podzol zone.

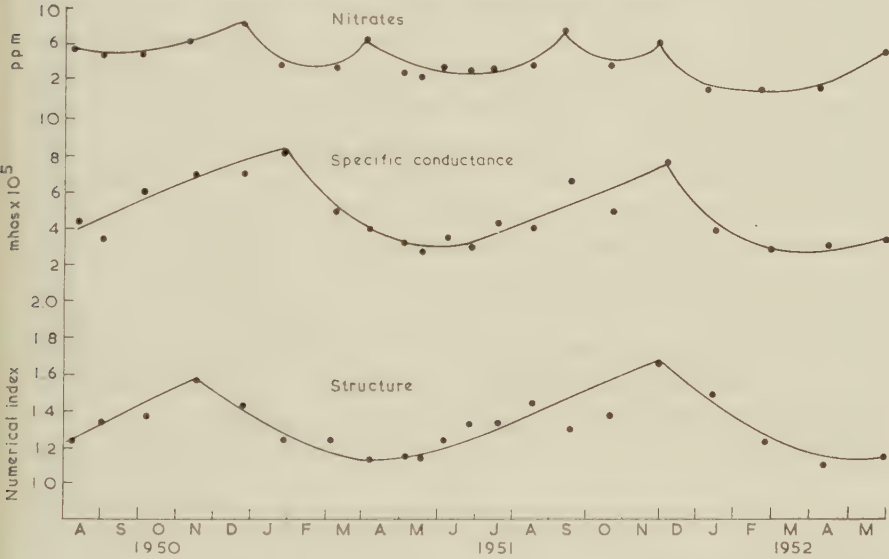


Fig. 1. Seasonal fluctuations of structural index, specific conductance, and nitrates of Chester loam.

The structure and specific conductance curves have peaks in late fall and low points in late winter and early spring. In a large measure, the conductance, which measures the electrolyte content, is a product of the third element of soil conditions, namely the biological element.

As the summer season ends there is little vegetative growth and plants put little demand on the soil for nutrients. At the same time,

the processes of humification and mineralization of plant residues increase the humate and electrolyte contents, especially in the rhizosphere. It should be noted that the peaks on the structure curve as well as on the conductance curve occur long after the growing season has ended. This would tend to minimize the effect of root action as the dominant force in producing structure in fall. The late fall and winter rains remove the electrolytes (perhaps also the humates that were stabilized in the soil by the bases). With the awakening of spring, the paucity of available plant residues precludes the rapid formation and accumulation of electrolytes. At the same time, the active plant growth puts a heavy demand on the soil for nutrients, and hence the low point on the conductance curve. In addition, it takes the entire growing season to regenerate the structure that deteriorates during the winter.

The nitrate curve shows some correlation with that of the conductance, but data on nitrates cannot be relied upon as an index of it, and hence not of soil structure. It is well known that nitrate formation, utilization, and accumulation are unpredictable, even though generally they can be explained.

Data on pH of the soil-water extracts show a rise in fall, with Ca and K as the predominating bases. Very little soluble organic matter is present at that time in the soil-water extract. Formation of Ca-humates, which become readily insoluble under meteorologic conditions of the fall season, is responsible for that. It might be added that these humates undoubtedly contribute to the stability of structure, as discussed elsewhere (J o f f e ³), p. 130).

CONCLUSION

The significance of specific conductance of soil water extracts as an index of soil structure lies in the possibility of studying structural changes in natural and lightly fertilized soils of the temperate climate.

Experience with heavily fertilized truck garden soils shows some departure from the curves given, because of excess of electrolytes. The general trends, however, can be easily followed.

SUGGESTIONS

In the zone of podzolization, the improved structure attained in the fall and subject to deterioration during the winter may be maintained by increasing the electrolyte content during the critical periods. The beneficial effects of cover crops are in some measure due to the prevention of losses of electrolytes by leaching.

Many years of experience by the senior author in maintaining a high electrolyte content in soils heavier than loamy sands by the addition of a mixture of dolomitic limestone, gypsum, Epsom salt, and superphosphate have proven to be a powerful expedient in preventing the deterioration of the improved structure of the fall season. This practice paid off in higher crop yields³).

While on the subject of structure improvement, the senior author would suggest to look into the feasibility of simulating in the zone of podzolization some conditions prevailing in the chernozem type of soil formation where structure is continuous and apparently independent of the electrolyte content at any particular season.

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BEMERKUNGEN ZUR AUSDEUTUNG VON BLATTANALYSEN

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Die bekannten Unzulänglichkeiten der chemischen Bodenuntersuchungsmethoden und die Umständlichkeit von Feld- und Gefäßversuchen haben Veranlassung gegeben, in Fortführung älterer Versuche (Literaturzusammenstellung bei Goodall und Gregory²⁾) die Nährelementkonzentration in der Pflanze zur Grundlage einer ökologischen Inventur (für die praktische Landwirtschaft = Bestimmung des Düngedarfs) zu machen. Über die Ausdeutung der analytisch ermittelten Werte herrscht offenbar z.T. noch einige Unklarheit. Auf einige Punkte sei in aller Kürze hingewiesen.

Die Bodenanalyse bestimmt einen mehr oder minder großen Anteil der Nährelemente im Boden und setzt voraus, daß diese Menge in einer bestimmten Beziehung zum Ernährungszustand der Pflanze steht. Die Blattanalyse (Nährelementkonzentration) dagegen hat das Ziel, direkt den Ernährungszustand der Pflanze zu ermitteln, um aus diesem auf den verfügbaren Nährelementgehalt des Bodens zu schließen.

Die Konzentration eines Nährelementes in einer Pflanze ist im wesentlichen abhängig

- 1) von der aufgenommenen Menge dieses Nährelements, diese wiederum von
 - a) verfügbarer Nährelementmenge im Boden
 - b) Wurzeleistung (Pflanzenart usw.)
 - c) Ionenwechselwirkungen (positiv und negativ)
 - d) Zeit
- und
- 2) von der produzierten Pflanzensubstanz, die wiederum abhängt von

a) Wachstumsstadium (Zeit)

b) Gunst der übrigen Wachstumsfaktoren.

Aus diesen Zusammenhängen ist ersichtlich, daß die Blattanalyse streng vergleichbare Werte nur dann liefert, wenn die Analysen an denselben Pflanzenarten (möglichst auch -sorten) im selben Wachstumsstadium bei gleicher Konstellation der anderen Wachstumsfaktoren durchgeführt werden (Unterschiede der Nährelementverteilung in der Pflanze sollen hier nicht diskutiert werden). Den Zeitfaktor kann man nicht eliminieren, da sich aufgenommene Nährelementmenge und Ertrag nicht in gleichem Ausmaß verändern. Vielmehr nimmt die Aufnahme in späteren Wachstumsstadien weniger zu als die Trockensubstanzbildung, so daß die Konzentration sinkt (auch durch Nährelement-Rückwanderung).

Die Anwendbarkeit der Blattanalyse setzt nun eine bestimmte Beziehung zwischen aufgenommener Nährelementmenge (1) und

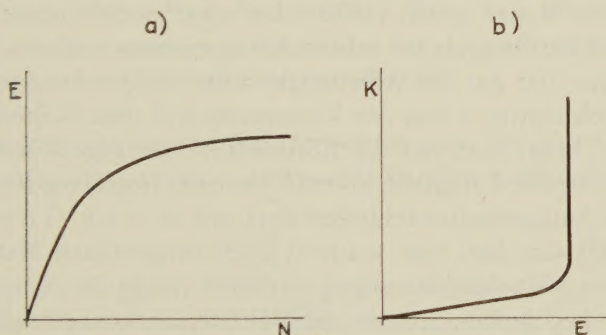


Fig. 1. a) Beziehung zwischen Nährelementmenge und Ertrag. b) Beziehung zwischen Nährelementkonzentration und Ertrag.

Ertrag (2) voraus. Diese besteht nach heute allgemein anerkannter Ansicht in Form einer logarithmischen Funktion (Mitscherlich-Kurve), sofern man annimmt, daß die steigenden Nährelementgaben (N) auch von der Pflanze aufgenommen werden (Fig. 1a). Dann besteht zwischen Ertrag (E) und Nährelementkonzentration (K) in der Pflanze eine Beziehung, die annähernd wie die zweite Kurve verläuft (Fig. 1b). Ausnahmen siehe Steenbjerg⁶⁾.

Die voraussichtliche Ertragssteigerung bei Düngung (und damit der Düngbedarf) ist also um so höher je geringer die Nährelementkonzentration ist, und eine Düngung beeinflusst im Minimumgebiet den Ertrag stärker als die Konzentration, im Maximumgebiet die

Konzentration stärker als den Ertrag (wenn also Scharer und Lemme⁵⁾ fanden, daß bei N-Düngung auf N-armem Boden die Ertragssteigerung mit $\approx 28,3\%$ die Spiegelwertsteigerung mit $\approx 9,7\%$ wesentlich überschritt, so steht das durchaus im Einklang mit der Theorie).

Aus der Übersicht ist abzuleiten, daß die Konzentration eines Nährelementes (x) durch steigende Mengen eines anderen (y) im wesentlichen auf zweierlei Weise gesenkt werden kann, nämlich 1) durch eine Verminderung der Aufnahme (Antagonismus als Adsorptionsverdrängung nach Burström¹⁾) und 2) durch eine Steigerung der Trockensubstanzproduktion (Verdünnungseffekt, „falscher Antagonismus“ nach Lundegårdh⁴⁾). Im ersteren Falle werden also — bei gleichem Ertrag — sowohl Konzentration als auch aufgenommene Menge von x durch y gesenkt, im letzteren — bei steigendem Ertrag — nur die Konzentration, während die aufgenommene Menge gleich bleibt oder sogar noch ansteigen kann. Ein Urteil darüber, ob ein echter Antagonismus vorliegt, läßt sich also nur aus der Art der Abhängigkeit der aufgenommenen Menge des Nährelementes x von der Versorgung mit dem Nährelement y gewinnen. Trägt man nur die Konzentrationen gegeneinander auf, so ist es zumindest fraglich, ob man aus einer negativen Korrelation auf einen Antagonismus schließen darf, wie es van Goor³⁾ tut.

Verf. hat aus dem von van Goor mitgeteilten Material die entzogenen Nährelementmengen errechnet (da in der Arbeit die Erträge für die Lärchen-Sprosse, die Nährelementkonzentrationen dagegen nur für die Nadeln angegeben werden, mußte von der Annahme ausgegangen werden, daß die Konzentrationen zumindest für Vergleichszwecke auch repräsentativ für die ganzen Pflanzen sind). Trägt man diese gegeneinander oder gegen die jeweiligen Gaben des anderen Nährelementes auf, so bekommt man ein von den Angaben des genannten Autors abweichendes Bild. Als Beispiel seien nur die Kurven für die Böden 376 (N-reich) und 359 (P-reich) dargestellt.

Man sieht also, daß nur beim Boden 376 ein Antagonismus zwischen N und P zu bestehen scheint, während beim Boden 359 die Tendenz vorherrscht, daß mit steigenden N-Gaben auch der P-Entzug steigt. Die negative Korrelation beim Boden 376 braucht jedoch nicht durch einen Antagonismus verursacht zu sein, sondern kann durch eine Ertragsdepression infolge steigender N-Gaben bedingt

sein (in der Fig. 2 werden die Kombinationen mit den Höchsterträgen durch Kreise markiert). Diesen Zusammenhang könnte man allenfalls als eine besondere Art von „metabolischem Antagonismus“ (Lundegårdh, l.c.) bezeichnen.

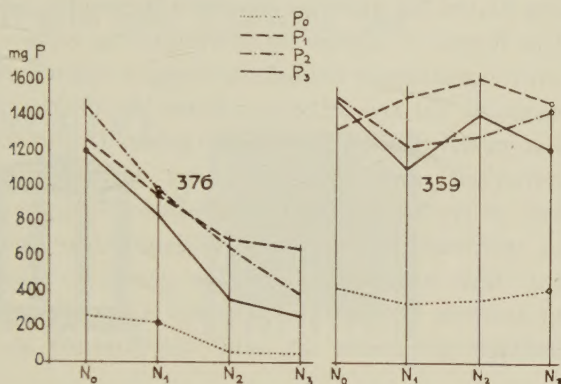


Fig. 2. Beziehungen zwischen N-Gaben und P-Entzug bei verschiedener P-Düngung von zwei Böden.

Will man den Einfluß des Nährelementes y auf die Aufnahme des Nährelementes x ermitteln, so darf man lediglich aus solchen Kurven

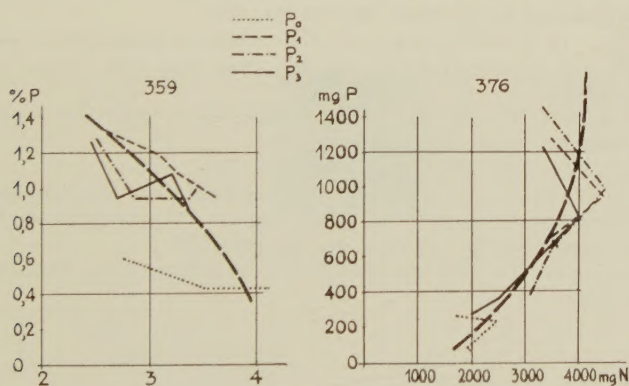


Fig. 3. a) Beziehungen zwischen N- und P-Konzentration bei verschiedener P-Düngung (Abszisse: %N). b) Beziehungen zwischen N- und P-Entzügen bei verschiedener P-Düngung.

Schlüsse ziehen, in denen nur y variiert wurde. Verbindet man in der von van Goor aufgezeigten Beziehung zwischen N- und P-Ge-

halt der Lärchennadeln beim Boden 359 die Punkte gleicher P-Düngung miteinander, so ergibt sich bei den einzelnen P-Stufen ein mit der gestrichelten Kurve (v a n G o o r) nicht völlig übereinstimmendes Bild (Fig. 3a). Verführe man bezüglich der P- und N-Entzüge beim Boden 376 in entsprechender Weise (Fig. 3b), so würde die gemittelte Kurve — sofern sie beweiskräftig wäre — den vom genannten Autor gezogenen Schlußfolgerungen widersprechen.

Die Blattanalyse hat zweifellos gegenüber der chemischen Bodenanalyse einige prinzipielle Vorteile (z.B. gehen Unterschiede in der Durchwurzelbarkeit und Hemmung der Nährelementaufnahme durch andere, in großen Mengen vorhandene Elemente in das Meßergebnis ein, während die chemische Bodenanalyse sie unberücksichtigt läßt). Ihre Ausdeutung ist aber genau so schwierig (z.B. Einfluß von anderen Wachstumsfaktoren). Ob sie zur Beurteilung des Düngbedarfes geeigneter ist, muß die Zukunft in der Praxis erweisen.

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